

PUZZLER

After this bottle of champagne was shaken, the cork was popped off and champagne spewed everywhere. Contrary to common belief, shaking a champagne bottle before opening it does not increase the pressure of the carbon dioxide (CO_2) inside. In fact, if you know the trick, you can open a thoroughly shaken bottle without spraying a drop. What's the secret? And why isn't the pressure inside the bottle greater after the bottle is shaken? (Steve Niedorf/The Image Bank)



chapter

19

Temperature

Chapter Outline


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In our study of mechanics, we carefully defined such concepts as mass, force, and kinetic energy to facilitate our quantitative approach. Likewise, a quantitative description of thermal phenomena requires a careful definition of such important terms as *temperature*, *heat*, and *internal energy*. This chapter begins with a look at these three entities and with a description of one of the laws of thermodynamics (the poetically named “zeroth law”). We then discuss the three most common temperature scales—Celsius, Fahrenheit, and Kelvin.

Next, we consider why the composition of a body is an important factor when we are dealing with thermal phenomena. For example, gases expand appreciably when heated, whereas liquids and solids expand only slightly. If a gas is not free to expand as it is heated, its pressure increases. Certain substances may melt, boil, burn, or explode when they are heated, depending on their composition and structure.

This chapter concludes with a study of ideal gases on the macroscopic scale. Here, we are concerned with the relationships among such quantities as pressure, volume, and temperature. Later on, in Chapter 21, we shall examine gases on a microscopic scale, using a model that represents the components of a gas as small particles.

19.1 TEMPERATURE AND THE ZEROTH LAW OF THERMODYNAMICS

 We often associate the concept of temperature with how hot or cold an object feels when we touch it. Thus, our senses provide us with a qualitative indication of temperature. However, our senses are unreliable and often mislead us. For example, if we remove a metal ice tray and a cardboard box of frozen vegetables from the freezer, the ice tray feels colder than the box even though both are at the same temperature. The two objects feel different because metal is a better thermal conductor than cardboard is. What we need, therefore, is a reliable and reproducible method for establishing the relative hotness or coldness of bodies. Scientists have developed a variety of thermometers for making such quantitative measurements.

We are all familiar with the fact that two objects at different initial temperatures eventually reach some intermediate temperature when placed in contact with each other. For example, when a scoop of ice cream is placed in a room-temperature glass bowl, the ice cream melts and the temperature of the bowl decreases. Likewise, when an ice cube is dropped into a cup of hot coffee, it melts and the coffee’s temperature decreases.

To understand the concept of temperature, it is useful to define two often-used phrases: *thermal contact* and *thermal equilibrium*. To grasp the meaning of thermal contact, let us imagine that two objects are placed in an insulated container such that they interact with each other but not with the rest of the world. If the objects are at different temperatures, energy is exchanged between them, even if they are initially not in physical contact with each other. **Heat is the transfer of energy from one object to another object as a result of a difference in temperature between the two.** We shall examine the concept of heat in greater detail in Chapter 20. For purposes of the current discussion, we assume that two objects are in **thermal contact** with each other if energy can be exchanged between them. **Thermal equilibrium** is a situation in which two objects in thermal contact with each other cease to exchange energy by the process of heat.

Let us consider two objects A and B, which are not in thermal contact, and a third object C, which is our thermometer. We wish to determine whether A and B



Molten lava flowing down a mountain in Kilauea, Hawaii. The temperature of the hot lava flowing from a central crater decreases until the lava is in thermal equilibrium with its surroundings. At that equilibrium temperature, the lava has solidified and formed the mountains.

QuickLab

Fill three cups with tap water: one hot, one cold, and one lukewarm. Dip your left index finger into the hot water and your right index finger into the cold water. Slowly count to 20, then quickly dip both fingers into the lukewarm water. What do you feel?

are in thermal equilibrium with each other. The thermometer (object C) is first placed in thermal contact with object A until thermal equilibrium is reached. From that moment on, the thermometer's reading remains constant, and we record this reading. The thermometer is then removed from object A and placed in thermal contact with object B. The reading is again recorded after thermal equilibrium is reached. If the two readings are the same, then object A and object B are in thermal equilibrium with each other.

We can summarize these results in a statement known as the **zeroth law of thermodynamics** (the law of equilibrium):

Zeroth law of thermodynamics

If objects A and B are separately in thermal equilibrium with a third object C, then objects A and B are in thermal equilibrium with each other.

This statement can easily be proved experimentally and is very important because it enables us to define temperature. We can think of **temperature** as the property that determines whether an object is in thermal equilibrium with other objects. **Two objects in thermal equilibrium with each other are at the same temperature.** Conversely, if two objects have different temperatures, then they are not in thermal equilibrium with each other.

19.2 THERMOMETERS AND THE CELSIUS TEMPERATURE SCALE

Thermometers are devices that are used to define and measure temperatures. All thermometers are based on the principle that some physical property of a system changes as the system's temperature changes. Some physical properties that change with temperature are (1) the volume of a liquid, (2) the length of a solid, (3) the pressure of a gas at constant volume, (4) the volume of a gas at constant pressure, (5) the electric resistance of a conductor, and (6) the color of an object. For a given substance and a given temperature range, a temperature scale can be established on the basis of any one of these physical properties.

A common thermometer in everyday use consists of a mass of liquid—usually mercury or alcohol—that expands into a glass capillary tube when heated (Fig. 19.1). In this case the physical property is the change in volume of a liquid. Any temperature change can be defined as being proportional to the change in length of the liquid column. The thermometer can be calibrated by placing it in thermal contact with some natural systems that remain at constant temperature. One such system is a mixture of water and ice in thermal equilibrium at atmospheric pressure. On the **Celsius temperature scale**, this mixture is defined to have a temperature of zero degrees Celsius, which is written as 0°C ; this temperature is called the *ice point* of water. Another commonly used system is a mixture of water and steam in thermal equilibrium at atmospheric pressure; its temperature is 100°C , which is the *steam point* of water. Once the liquid levels in the thermometer have been established at these two points, the distance between the two points is divided into 100 equal segments to create the Celsius scale. Thus, each segment denotes a change in temperature of one Celsius degree. (This temperature scale used to be called the *centigrade scale* because there are 100 gradations between the ice and steam points of water.)

Thermometers calibrated in this way present problems when extremely accurate readings are needed. For instance, the readings given by an alcohol ther-



Figure 19.1 As a result of thermal expansion, the level of the mercury in the thermometer rises as the mercury is heated by water in the test tube.

mometer calibrated at the ice and steam points of water might agree with those given by a mercury thermometer only at the calibration points. Because mercury and alcohol have different thermal expansion properties, when one thermometer reads a temperature of, for example, 50°C , the other may indicate a slightly different value. The discrepancies between thermometers are especially large when the temperatures to be measured are far from the calibration points.¹

An additional practical problem of any thermometer is the limited range of temperatures over which it can be used. A mercury thermometer, for example, cannot be used below the freezing point of mercury, which is -39°C , and an alcohol thermometer is not useful for measuring temperatures above 85°C , the boiling point of alcohol. To surmount this problem, we need a universal thermometer whose readings are independent of the substance used in it. The gas thermometer, discussed in the next section, approaches this requirement.

19.3 THE CONSTANT-VOLUME GAS THERMOMETER AND THE ABSOLUTE TEMPERATURE SCALE

The temperature readings given by a gas thermometer are nearly independent of the substance used in the thermometer. One version is the constant-volume gas thermometer shown in Figure 19.2. The physical change exploited in this device is the variation of pressure of a fixed volume of gas with temperature. When the constant-volume gas thermometer was developed, it was calibrated by using the ice

¹ Two thermometers that use the same liquid may also give different readings. This is due in part to difficulties in constructing uniform-bore glass capillary tubes.

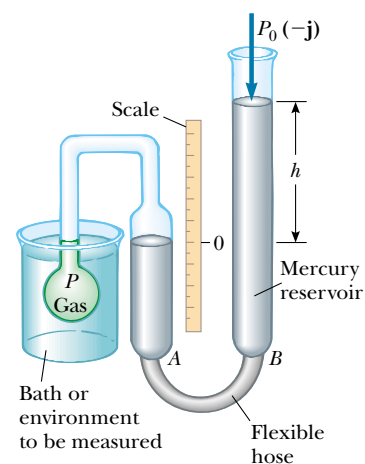


Figure 19.2 A constant-volume gas thermometer measures the pressure of the gas contained in the flask immersed in the bath. The volume of gas in the flask is kept constant by raising or lowering reservoir *B* to keep the mercury level in column *A* constant.

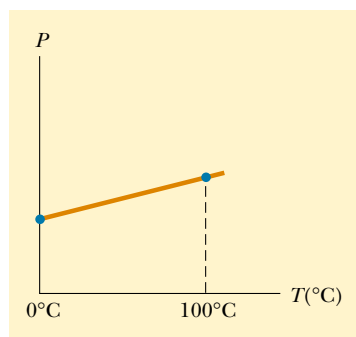


Figure 19.3 A typical graph of pressure versus temperature taken with a constant-volume gas thermometer. The two dots represent known reference temperatures (the ice and steam points of water).

and steam points of water, as follows (a different calibration procedure, which we shall discuss shortly, is now used): The flask was immersed in an ice bath, and mercury reservoir *B* was raised or lowered until the top of the mercury in column *A* was at the zero point on the scale. The height *h*, the difference between the mercury levels in reservoir *B* and column *A*, indicated the pressure in the flask at 0°C.

The flask was then immersed in water at the steam point, and reservoir *B* was readjusted until the top of the mercury in column *A* was again at zero on the scale; this ensured that the gas's volume was the same as it was when the flask was in the ice bath (hence, the designation “constant volume”). This adjustment of reservoir *B* gave a value for the gas pressure at 100°C. These two pressure and temperature values were then plotted, as shown in Figure 19.3. The line connecting the two points serves as a calibration curve for unknown temperatures. If we wanted to measure the temperature of a substance, we would place the gas flask in thermal contact with the substance and adjust the height of reservoir *B* until the top of the mercury column in *A* was at zero on the scale. The height of the mercury column would indicate the pressure of the gas; knowing the pressure, we could find the temperature of the substance using the graph in Figure 19.3.



10.3

Now let us suppose that temperatures are measured with gas thermometers containing different gases at different initial pressures. Experiments show that the thermometer readings are nearly independent of the type of gas used, as long as the gas pressure is low and the temperature is well above the point at which the gas liquefies (Fig. 19.4). The agreement among thermometers using various gases improves as the pressure is reduced.

If you extend the curves shown in Figure 19.4 toward negative temperatures, you find, in every case, that the pressure is zero when the temperature is -273.15°C . This significant temperature is used as the basis for the **absolute temperature scale**, which sets -273.15°C as its zero point. This temperature is often referred to as **absolute zero**. The size of a degree on the absolute temperature scale is identical to the size of a degree on the Celsius scale. Thus, the conversion between these temperatures is

$$T_C = T - 273.15 \quad (19.1)$$

where T_C is the Celsius temperature and T is the absolute temperature.

Because the ice and steam points are experimentally difficult to duplicate, an absolute temperature scale based on a single fixed point was adopted in 1954 by the International Committee on Weights and Measures. From a list of fixed points associated with various substances (Table 19.1), the triple point of water was chosen as the reference temperature for this new scale. The **triple point of water** is the single combination of temperature and pressure at which liquid water, gaseous

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For more information about the temperature standard, visit the National Institute of Standards and Technology at <http://www.nist.gov>

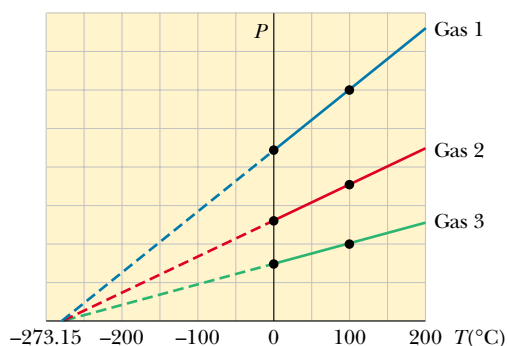


Figure 19.4 Pressure versus temperature for three dilute gases. Note that, for all gases, the pressure extrapolates to zero at the temperature -273.15°C .

TABLE 19.1 Fixed-Point Temperatures^a

Fixed Point	Temperature (°C)	Temperature (K)
Triple point of hydrogen	− 259.34	13.81
Boiling point of helium	− 268.93	4.215
Boiling point of hydrogen at 33.36 kPa pressure	− 256.108	17.042
Boiling point of hydrogen	− 252.87	20.28
Triple point of neon	− 246.048	27.102
Triple point of oxygen	− 218.789	54.361
Boiling point of oxygen	− 182.962	90.188
Triple point of water	0.01	273.16
Boiling point of water	100.00	373.15
Freezing point of tin	231.968 1	505.118 1
Freezing point of zinc	419.58	692.73
Freezing point of silver	961.93	1 235.08
Freezing point of gold	1 064.43	1 337.58

^aAll values are from National Bureau of Standards Special Publication 420; U. S. Department of Commerce, May 1975. All values are at standard atmospheric pressure except for triple points and as noted.

water, and ice (solid water) coexist in equilibrium. This triple point occurs at a temperature of approximately 0.01°C and a pressure of 4.58 mm of mercury. On the new scale, which uses the unit *kelvin*, the temperature of water at the triple point was set at 273.16 kelvin, abbreviated 273.16 K. (*Note:* no degree sign “°” is used with the unit kelvin.) This choice was made so that the old absolute temperature scale based on the ice and steam points would agree closely with the new scale based on the triple point. This new absolute temperature scale (also called the **Kelvin scale**) employs the SI unit of absolute temperature, the **kelvin**, which is defined to be **1/273.16 of the difference between absolute zero and the temperature of the triple point of water.**

Figure 19.5 shows the absolute temperature for various physical processes and structures. The temperature of absolute zero (0 K) cannot be achieved, although laboratory experiments incorporating the laser cooling of atoms have come very close.

What would happen to a gas if its temperature could reach 0 K? As Figure 19.4 indicates, the pressure it exerts on the walls of its container would be zero. In Section 19.5 we shall show that the pressure of a gas is proportional to the average kinetic energy of its molecules. Thus, according to classical physics, the kinetic energy of the gas molecules would become zero at absolute zero, and molecular motion would cease; hence, the molecules would settle out on the bottom of the container. Quantum theory modifies this model and shows that some residual energy, called the *zero-point energy*, would remain at this low temperature.

The Celsius, Fahrenheit, and Kelvin Temperature Scales²

Equation 19.1 shows that the Celsius temperature T_C is shifted from the absolute (Kelvin) temperature T by 273.15°. Because the size of a degree is the same on the

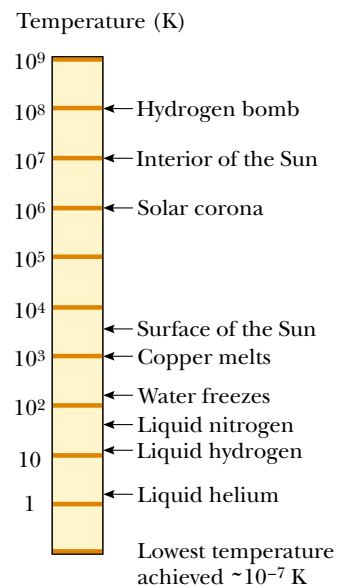


Figure 19.5 Absolute temperatures at which various physical processes occur. Note that the scale is logarithmic.

² Named after Anders Celsius (1701–1744), Gabriel Fahrenheit (1686–1736), and William Thomson, Lord Kelvin (1824–1907), respectively.

two scales, a temperature difference of 5°C is equal to a temperature difference of 5 K. The two scales differ only in the choice of the zero point. Thus, the ice-point temperature on the Kelvin scale, 273.15 K, corresponds to 0.00°C , and the Kelvin-scale steam point, 373.15 K, is equivalent to 100.00°C .

A common temperature scale in everyday use in the United States is the **Fahrenheit scale**. This scale sets the temperature of the ice point at 32°F and the temperature of the steam point at 212°F . The relationship between the Celsius and Fahrenheit temperature scales is

$$T_{\text{F}} = \frac{9}{5}T_{\text{C}} + 32^{\circ}\text{F} \quad (19.2)$$

Quick Quiz 19.1

What is the physical significance of the factor $\frac{9}{5}$ in Equation 19.2? Why is this factor missing in Equation 19.1?

Extending the ideas considered in Quick Quiz 19.1, we use Equation 19.2 to find a relationship between changes in temperature on the Celsius, Kelvin, and Fahrenheit scales:

$$\Delta T_{\text{C}} = \Delta T = \frac{5}{9}\Delta T_{\text{F}} \quad (19.3)$$

EXAMPLE 19.1 Converting Temperatures

On a day when the temperature reaches 50°F , what is the temperature in degrees Celsius and in kelvins?

Solution Substituting $T_{\text{F}} = 50^{\circ}\text{F}$ into Equation 19.2, we obtain

$$T_{\text{C}} = \frac{5}{9}(T_{\text{F}} - 32) = \frac{5}{9}(50 - 32) = 10^{\circ}\text{C}$$

From Equation 19.1, we find that

$$T = T_{\text{C}} + 273.15 = 10^{\circ}\text{C} + 273.15 = 283 \text{ K}$$

A convenient set of weather-related temperature equivalents to keep in mind is that 0°C is (literally) freezing at 32°F , 10°C is cool at 50°F , 30°C is warm at 86°F , and 40°C is a hot day at 104°F .

EXAMPLE 19.2 Heating a Pan of Water

A pan of water is heated from 25°C to 80°C . What is the change in its temperature on the Kelvin scale and on the Fahrenheit scale?

Solution From Equation 19.3, we see that the change in temperature on the Celsius scale equals the change on the Kelvin scale. Therefore,

$$\Delta T = \Delta T_{\text{C}} = 80^{\circ}\text{C} - 25^{\circ}\text{C} = 55^{\circ}\text{C} = 55 \text{ K}$$

From Equation 19.3, we also find that

$$\Delta T_{\text{F}} = \frac{9}{5}\Delta T_{\text{C}} = \frac{9}{5}(55^{\circ}\text{C}) = 99^{\circ}\text{F}$$

19.4 THERMAL EXPANSION OF SOLIDS AND LIQUIDS

Our discussion of the liquid thermometer made use of one of the best-known changes in a substance: As its temperature increases, its volume almost always increases. (As we shall see shortly, in some substances the volume decreases when the temperature increases.) This phenomenon, known as **thermal expansion**, has

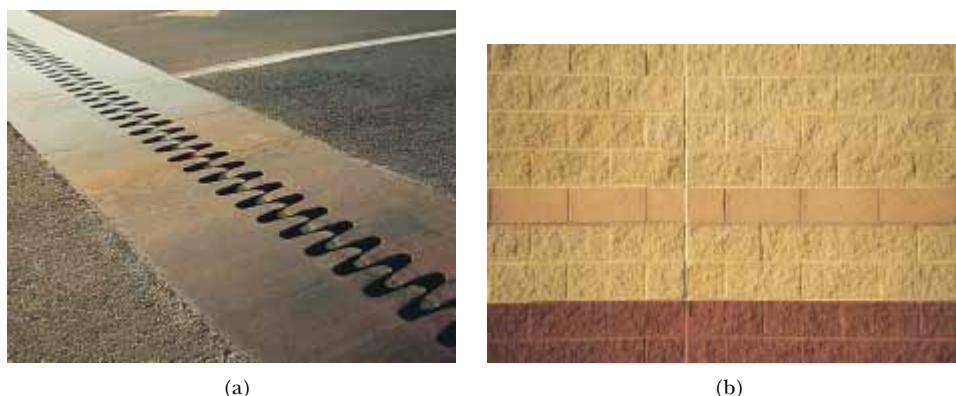


Figure 19.6 (a) Thermal-expansion joints are used to separate sections of roadways on bridges. Without these joints, the surfaces would buckle due to thermal expansion on very hot days or crack due to contraction on very cold days. (b) The long, vertical joint is filled with a soft material that allows the wall to expand and contract as the temperature of the bricks changes.

an important role in numerous engineering applications. For example, thermal-expansion joints, such as those shown in Figure 19.6, must be included in buildings, concrete highways, railroad tracks, brick walls, and bridges to compensate for dimensional changes that occur as the temperature changes.

Thermal expansion is a consequence of the change in the average separation between the constituent atoms in an object. To understand this, imagine that the atoms are connected by stiff springs, as shown in Figure 19.7. At ordinary temperatures, the atoms in a solid oscillate about their equilibrium positions with an amplitude of approximately 10^{-11} m and a frequency of approximately 10^{13} Hz. The average spacing between the atoms is about 10^{-10} m. As the temperature of the solid increases, the atoms oscillate with greater amplitudes; as a result, the average separation between them increases.³ Consequently, the object expands.

If thermal expansion is sufficiently small relative to an object's initial dimensions, the change in any dimension is, to a good approximation, proportional to the first power of the temperature change. Suppose that an object has an initial length L_i along some direction at some temperature and that the length increases by an amount ΔL for a change in temperature ΔT . Because it is convenient to consider the fractional change in length per degree of temperature change, we define the **average coefficient of linear expansion** as

$$\alpha \equiv \frac{\Delta L/L_i}{\Delta T}$$

Experiments show that α is constant for small changes in temperature. For purposes of calculation, this equation is usually rewritten as

$$\Delta L = \alpha L_i \Delta T \quad (19.4)$$

or as

$$L_f - L_i = \alpha L_i (T_f - T_i) \quad (19.5)$$

³ More precisely, thermal expansion arises from the *asymmetrical* nature of the potential-energy curve for the atoms in a solid. If the oscillators were truly harmonic, the average atomic separations would not change regardless of the amplitude of vibration.

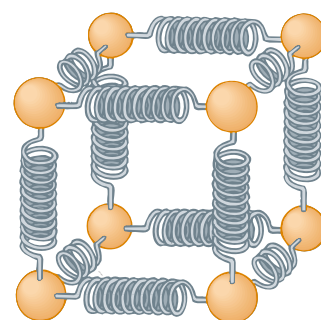


Figure 19.7 A mechanical model of the atomic configuration in a substance. The atoms (spheres) are imagined to be attached to each other by springs that reflect the elastic nature of the interatomic forces.

Average coefficient of linear expansion

The change in length of an object is proportional to the change in temperature

where L_f is the final length, T_i and T_f are the initial and final temperatures, and the proportionality constant α is the average coefficient of linear expansion for a given material and has units of $^{\circ}\text{C}^{-1}$.

It may be helpful to think of thermal expansion as an effective magnification or as a photographic enlargement of an object. For example, as a metal washer is heated (Fig. 19.8), all dimensions, including the radius of the hole, increase according to Equation 19.4.

Table 19.2 lists the average coefficient of linear expansion for various materials. Note that for these materials α is positive, indicating an increase in length with increasing temperature. This is not always the case. Some substances—calcite (CaCO_3) is one example—expand along one dimension (positive α) and contract along another (negative α) as their temperatures are increased.

Because the linear dimensions of an object change with temperature, it follows that surface area and volume change as well. The change in volume at constant pressure is proportional to the initial volume V_i and to the change in temperature according to the relationship

$$\Delta V = \beta V_i \Delta T \quad (19.6)$$

where β is the **average coefficient of volume expansion**. For a solid, the average coefficient of volume expansion is approximately three times the average linear expansion coefficient: $\beta = 3\alpha$. (This assumes that the average coefficient of linear expansion of the solid is the same in all directions.)

To see that $\beta = 3\alpha$ for a solid, consider a box of dimensions ℓ , w , and h . Its volume at some temperature T_i is $V_i = \ell wh$. If the temperature changes to $T_i + \Delta T$, its volume changes to $V_i + \Delta V$, where each dimension changes according to Equation 19.4. Therefore,

$$\begin{aligned} V_i + \Delta V &= (\ell + \Delta\ell)(w + \Delta w)(h + \Delta h) \\ &= (\ell + \alpha\ell\Delta T)(w + \alpha w\Delta T)(h + \alpha h\Delta T) \\ &= \ell wh(1 + \alpha\Delta T)^3 \\ &= V_i[1 + 3\alpha\Delta T + 3(\alpha\Delta T)^2 + (\alpha\Delta T)^3] \end{aligned}$$

The change in volume of a solid at constant pressure is proportional to the change in temperature

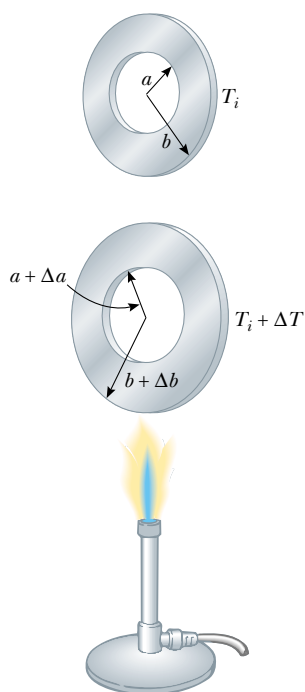


Figure 19.8 Thermal expansion of a homogeneous metal washer. As the washer is heated, all dimensions increase. (The expansion is exaggerated in this figure.)

TABLE 19.2 Average Expansion Coefficients for Some Materials Near Room Temperature

Material	Average Linear Expansion Coefficient (α) ($^{\circ}\text{C}^{-1}$)	Material	Average Volume Expansion Coefficient (β) ($^{\circ}\text{C}^{-1}$)
Aluminum	24×10^{-6}	Alcohol, ethyl	1.12×10^{-4}
Brass and bronze	19×10^{-6}	Benzene	1.24×10^{-4}
Copper	17×10^{-6}	Acetone	1.5×10^{-4}
Glass (ordinary)	9×10^{-6}	Glycerin	4.85×10^{-4}
Glass (Pyrex)	3.2×10^{-6}	Mercury	1.82×10^{-4}
Lead	29×10^{-6}	Turpentine	9.0×10^{-4}
Steel	11×10^{-6}	Gasoline	9.6×10^{-4}
Invar (Ni–Fe alloy)	0.9×10^{-6}	Air at 0°C	3.67×10^{-3}
Concrete	12×10^{-6}	Helium	3.665×10^{-3}

If we now divide both sides by V_i and then isolate the term $\Delta V/V_i$, we obtain the fractional change in volume:

$$\frac{\Delta V}{V_i} = 3\alpha \Delta T + 3(\alpha \Delta T)^2 + (\alpha \Delta T)^3$$

Because $\alpha \Delta T \ll 1$ for typical values of ΔT ($< \sim 100^\circ\text{C}$), we can neglect the terms $3(\alpha \Delta T)^2$ and $(\alpha \Delta T)^3$. Upon making this approximation, we see that

$$\frac{\Delta V}{V_i} = 3\alpha \Delta T$$

$$3\alpha = \frac{1}{V_i} \frac{\Delta V}{\Delta T}$$

Equation 19.6 shows that the right side of this expression is equal to β , and so we have $3\alpha = \beta$, the relationship we set out to prove. In a similar way, you can show that the change in area of a rectangular plate is given by $\Delta A = 2\alpha A_i \Delta T$ (see Problem 53).

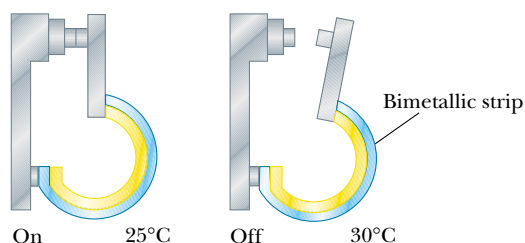
As Table 19.2 indicates, each substance has its own characteristic average coefficient of expansion. For example, when the temperatures of a brass rod and a steel rod of equal length are raised by the same amount from some common initial value, the brass rod expands more than the steel rod does because brass has a greater average coefficient of expansion than steel does. A simple mechanism called a *bimetallic strip* utilizes this principle and is found in practical devices such as thermostats. It consists of two thin strips of dissimilar metals bonded together. As the temperature of the strip increases, the two metals expand by different amounts and the strip bends, as shown in Figure 19.9.

QuickLab

Tape two plastic straws tightly together along their entire length but with a 2-cm offset. Hold them in a stream of very hot water from a faucet so that water pours through one but not through the other. Quickly hold the straws up and sight along their length. You should be able to see a very slight curvature in the tape caused by the difference in expansion of the two straws. The effect is small, so look closely. Running cold water through the same straw and again sighting along the length will help you see the small change in shape more clearly.



(a)



(b)



(c)

Figure 19.9 (a) A bimetallic strip bends as the temperature changes because the two metals have different expansion coefficients. (b) A bimetallic strip used in a thermostat to break or make electrical contact. (c) The interior of a thermostat, showing the coiled bimetallic strip. Why do you suppose the strip is coiled?

Quick Quiz 19.2

If you quickly plunge a room-temperature thermometer into very hot water, the mercury level will go *down* briefly before going up to a final reading. Why?

Quick Quiz 19.3

You are offered a prize for making the most sensitive glass thermometer using the materials in Table 19.2. Which glass and which working liquid would you choose?

EXAMPLE 19.3 Expansion of a Railroad Track

A steel railroad track has a length of 30.000 m when the temperature is 0.0°C. (a) What is its length when the temperature is 40.0°C?



Thermal expansion: The extreme temperature of a July day in Asbury Park, NJ, caused these railroad tracks to buckle and derail the train in the distance. (AP/Wide World Photos)

Solution Making use of Table 19.2 and noting that the change in temperature is 40.0°C, we find that the increase in length is

$$\Delta L = \alpha L_i \Delta T = [11 \times 10^{-6} (\text{°C})^{-1}] (30.000 \text{ m}) (40.0 \text{ °C}) = 0.013 \text{ m}$$

If the track is 30.000 m long at 0.0°C, its length at 40.0°C is **30.013 m.**

(b) Suppose that the ends of the rail are rigidly clamped at 0.0°C so that expansion is prevented. What is the thermal stress set up in the rail if its temperature is raised to 40.0°C?

Solution From the definition of Young's modulus for a solid (see Eq. 12.6), we have

$$\text{Tensile stress} = \frac{F}{A} = Y \frac{\Delta L}{L_i}$$

Because Y for steel is $20 \times 10^{10} \text{ N/m}^2$ (see Table 12.1), we have

$$\frac{F}{A} = (20 \times 10^{10} \text{ N/m}^2) \left(\frac{0.013 \text{ m}}{30.000 \text{ m}} \right) = \mathbf{8.7 \times 10^7 \text{ N/m}^2}$$

Exercise If the rail has a cross-sectional area of 30.0 cm², what is the force of compression in the rail?

Answer $2.6 \times 10^5 \text{ N} = 58\,000 \text{ lb!}$

The Unusual Behavior of Water

Liquids generally increase in volume with increasing temperature and have average coefficients of volume expansion about ten times greater than those of solids. Water is an exception to this rule, as we can see from its density-versus-temperature curve shown in Figure 19.10. As the temperature increases from 0°C to 4°C, water contracts and thus its density increases. Above 4°C, water expands with increasing temperature, and so its density decreases. In other words, the density of water reaches a maximum value of 1 000 kg/m³ at 4°C.

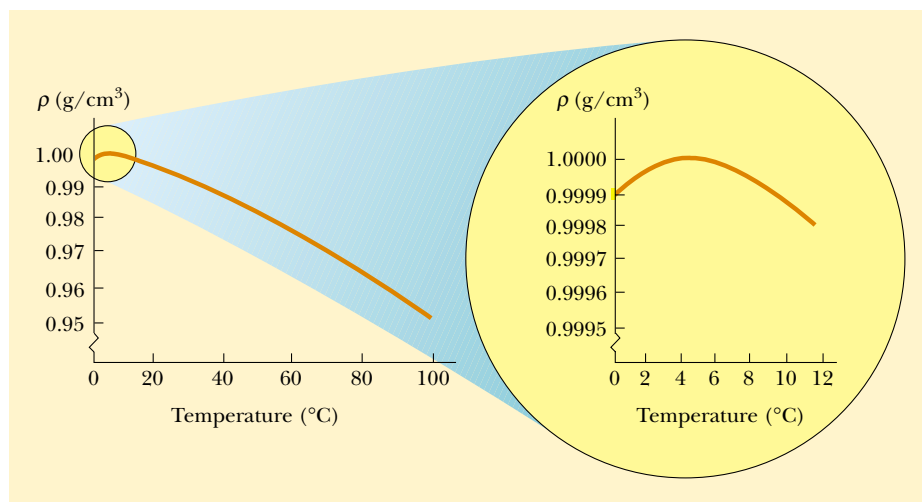


Figure 19.10 How the density of water at atmospheric pressure changes with temperature. The inset at the right shows that the maximum density of water occurs at 4°C.

We can use this unusual thermal-expansion behavior of water to explain why a pond begins freezing at the surface rather than at the bottom. When the atmospheric temperature drops from, for example, 7°C to 6°C, the surface water also cools and consequently decreases in volume. This means that the surface water is denser than the water below it, which has not cooled and decreased in volume. As a result, the surface water sinks, and warmer water from below is forced to the surface to be cooled. When the atmospheric temperature is between 4°C and 0°C, however, the surface water expands as it cools, becoming less dense than the water below it. The mixing process stops, and eventually the surface water freezes. As the water freezes, the ice remains on the surface because ice is less dense than water. The ice continues to build up at the surface, while water near the bottom remains at 4°C. If this were not the case, then fish and other forms of marine life would not survive.

19.5 MACROSCOPIC DESCRIPTION OF AN IDEAL GAS

10.5 In this section we examine the properties of a gas of mass m confined to a container of volume V at a pressure P and a temperature T . It is useful to know how these quantities are related. In general, the equation that interrelates these quantities, called the *equation of state*, is very complicated. However, if the gas is maintained at a very low pressure (or low density), the equation of state is quite simple and can be found experimentally. Such a low-density gas is commonly referred to as an *ideal gas*.⁴

⁴ To be more specific, the assumption here is that the temperature of the gas must not be too low (the gas must not condense into a liquid) or too high, and that the pressure must be low. In reality, an ideal gas does not exist. However, the concept of an ideal gas is very useful in view of the fact that real gases at low pressures behave as ideal gases do. The concept of an ideal gas implies that the gas molecules do not interact except upon collision, and that the molecular volume is negligible compared with the volume of the container.

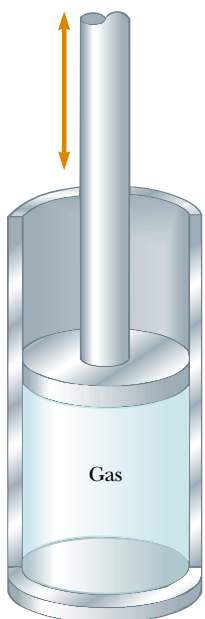


Figure 19.11 An ideal gas confined to a cylinder whose volume can be varied by means of a movable piston.

The universal gas constant

QuickLab

Vigorously shake a can of soda pop and then thoroughly tap its bottom and sides to dislodge any bubbles trapped there. You should be able to open the can without spraying its contents all over.

It is convenient to express the amount of gas in a given volume in terms of the number of moles n . As we learned in Section 1.3, one mole of any substance is that amount of the substance that contains Avogadro's number $N_A = 6.022 \times 10^{23}$ of constituent particles (atoms or molecules). The number of moles n of a substance is related to its mass m through the expression

$$n = \frac{m}{M} \quad (19.7)$$

where M is the molar mass of the substance (see Section 1.3), which is usually expressed in units of grams per mole (g/mol). For example, the molar mass of oxygen (O_2) is 32.0 g/mol. Therefore, the mass of one mole of oxygen is 32.0 g.

Now suppose that an ideal gas is confined to a cylindrical container whose volume can be varied by means of a movable piston, as shown in Figure 19.11. If we assume that the cylinder does not leak, the mass (or the number of moles) of the gas remains constant. For such a system, experiments provide the following information: First, when the gas is kept at a constant temperature, its pressure is inversely proportional to its volume (Boyle's law). Second, when the pressure of the gas is kept constant, its volume is directly proportional to its temperature (the law of Charles and Gay-Lussac). These observations are summarized by the **equation of state for an ideal gas**:

$$PV = nRT \quad (19.8)$$

In this expression, known as the **ideal gas law**, R is a universal constant that is the same for all gases and T is the absolute temperature in kelvins. Experiments on numerous gases show that as the pressure approaches zero, the quantity PV/nT approaches the same value R for all gases. For this reason, R is called the **universal gas constant**. In SI units, in which pressure is expressed in pascals ($1 \text{ Pa} = 1 \text{ N/m}^2$) and volume in cubic meters, the product PV has units of newton·meters, or joules, and R has the value

$$R = 8.315 \text{ J/mol} \cdot \text{K} \quad (19.9)$$

If the pressure is expressed in atmospheres and the volume in liters ($1 \text{ L} = 10^3 \text{ cm}^3 = 10^{-3} \text{ m}^3$), then R has the value

$$R = 0.08214 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$$

Using this value of R and Equation 19.8, we find that the volume occupied by 1 mol of any gas at atmospheric pressure and at 0°C (273 K) is 22.4 L.

Now that we have presented the equation of state, we are ready for a formal definition of an ideal gas: **An ideal gas is one for which PV/nT is constant at all pressures.**

The ideal gas law states that if the volume and temperature of a fixed amount of gas do not change, then the pressure also remains constant. Consider the bottle of champagne shown at the beginning of this chapter. Because the temperature of the bottle and its contents remains constant, so does the pressure, as can be shown by replacing the cork with a pressure gauge. Shaking the bottle displaces some carbon dioxide gas from the "head space" to form bubbles within the liquid, and these bubbles become attached to the inside of the bottle. (No new gas is generated by shaking.) When the bottle is opened, the pressure is reduced; this causes the volume of the bubbles to increase suddenly. If the bubbles are attached to the bottle (beneath the liquid surface), their rapid expansion expels liquid from the

bottle. If the sides and bottom of the bottle are first tapped until no bubbles remain beneath the surface, then when the champagne is opened, the drop in pressure will not force liquid from the bottle. Try the QuickLab, but practice before demonstrating to a friend!

The ideal gas law is often expressed in terms of the total number of molecules N . Because the total number of molecules equals the product of the number of moles n and Avogadro's number N_A , we can write Equation 19.8 as

$$PV = nRT = \frac{N}{N_A} RT$$

$$PV = Nk_B T \quad (19.10)$$

where k_B is **Boltzmann's constant**, which has the value

$$k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K} \quad (19.11)$$

Boltzmann's constant

It is common to call quantities such as P , V , and T the **thermodynamic variables** of an ideal gas. If the equation of state is known, then one of the variables can always be expressed as some function of the other two.

EXAMPLE 19.4 How Many Gas Molecules in a Container?

An ideal gas occupies a volume of 100 cm^3 at 20°C and 100 Pa . Find the number of moles of gas in the container.

Solution The quantities given are volume, pressure, and temperature: $V = 100 \text{ cm}^3 = 1.00 \times 10^{-4} \text{ m}^3$, $P = 100 \text{ Pa}$, and $T = 20^\circ\text{C} = 293 \text{ K}$. Using Equation 19.8, we find that

$$n = \frac{PV}{RT} = \frac{(100 \text{ Pa})(10^{-4} \text{ m}^3)}{(8.315 \text{ J/mol} \cdot \text{K})(293 \text{ K})} = 4.10 \times 10^{-6} \text{ mol}$$

Exercise How many molecules are in the container?

Answer 2.47×10^{18} molecules.

EXAMPLE 19.5 Filling a Scuba Tank

A certain scuba tank is designed to hold 66 ft^3 of air when it is at atmospheric pressure at 22°C . When this volume of air is compressed to an absolute pressure of $3\,000 \text{ lb/in.}^2$ and stored in a 10-L (0.35-ft^3) tank, the air becomes so hot that the tank must be allowed to cool before it can be used. If the air does not cool, what is its temperature? (Assume that the air behaves like an ideal gas.)

Solution If no air escapes from the tank during filling, then the number of moles n remains constant; therefore, using $PV = nRT$, and with n and R being constant, we obtain for the initial and final values:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

The initial pressure of the air is 14.7 lb/in.^2 , its final pressure is $3\,000 \text{ lb/in.}^2$, and the air is compressed from an initial volume of 66 ft^3 to a final volume of 0.35 ft^3 . The initial temperature, converted to SI units, is 295 K . Solving for T_f , we obtain

$$T_f = \left(\frac{P_f V_f}{P_i V_i} \right) T_i = \frac{(3\,000 \text{ lb/in.}^2)(0.35 \text{ ft}^3)}{(14.7 \text{ lb/in.}^2)(66 \text{ ft}^3)} (295 \text{ K})$$

$$= 319 \text{ K}$$

Exercise What is the air temperature in degrees Celsius and in degrees Fahrenheit?

Answer 45.9°C ; 115°F .

Quick Quiz 19.4

In the previous example we used SI units for the temperature in our calculation step but not for the pressures or volumes. When working with the ideal gas law, how do you decide when it is necessary to use SI units and when it is not?

EXAMPLE 19.6 Heating a Spray Can

A spray can containing a propellant gas at twice atmospheric pressure (202 kPa) and having a volume of 125 cm³ is at 22°C. It is then tossed into an open fire. When the temperature of the gas in the can reaches 195°C, what is the pressure inside the can? Assume any change in the volume of the can is negligible.

Solution We employ the same approach we used in Example 19.5, starting with the expression

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

Because the initial and final volumes of the gas are assumed to be equal, this expression reduces to

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

Solving for P_f gives

$$P_f = \left(\frac{T_f}{T_i}\right)(P_i) = \left(\frac{468 \text{ K}}{295 \text{ K}}\right)(202 \text{ kPa}) = 320 \text{ kPa}$$

Obviously, the higher the temperature, the higher the pressure exerted by the trapped gas. Of course, if the pressure increases high enough, the can will explode. Because of this possibility, you should never dispose of spray cans in a fire.

SUMMARY

Two bodies are in **thermal equilibrium** with each other if they have the same temperature.

The **zeroth law of thermodynamics** states that if objects A and B are separately in thermal equilibrium with a third object C, then objects A and B are in thermal equilibrium with each other.

The SI unit of absolute temperature is the **kelvin**, which is defined to be the fraction 1/273.16 of the temperature of the triple point of water.

When the temperature of an object is changed by an amount ΔT , its length changes by an amount ΔL that is proportional to ΔT and to its initial length L_i :

$$\Delta L = \alpha L_i \Delta T \quad (19.4)$$

where the constant α is the **average coefficient of linear expansion**. The **average volume expansion coefficient** β for a solid is approximately equal to 3α .

An **ideal gas** is one for which PV/nT is constant at all pressures. An ideal gas is described by the **equation of state**,

$$PV = nRT \quad (19.8)$$

where n equals the number of moles of the gas, V is its volume, R is the universal gas constant (8.315 J/mol·K), and T is the absolute temperature. A real gas behaves approximately as an ideal gas if it is far from liquefaction.

QUESTIONS

- Is it possible for two objects to be in thermal equilibrium if they are not in contact with each other? Explain.
- A piece of copper is dropped into a beaker of water. If the water's temperature increases, what happens to the temperature of the copper? Under what conditions are the water and copper in thermal equilibrium?
- In principle, any gas can be used in a constant-volume gas thermometer. Why is it not possible to use oxygen for temperatures as low as 15 K? What gas would you use? (Refer to the data in Table 19.1.)
- Rubber has a negative average coefficient of linear expansion. What happens to the size of a piece of rubber as it is warmed?
- Why should the amalgam used in dental fillings have the same average coefficient of expansion as a tooth? What would occur if they were mismatched?
- Explain why the thermal expansion of a spherical shell made of a homogeneous solid is equivalent to that of a solid sphere of the same material.
- A steel ring bearing has an inside diameter that is 0.1 mm smaller than the diameter of an axle. How can it be made to fit onto the axle without removing any material?
- Markings to indicate length are placed on a steel tape in a room that has a temperature of 22°C. Are measurements made with the tape on a day when the temperature is 27°C greater than, less than, or the same length as the object's length? Defend your answer.
- Determine the number of grams in 1 mol of each of the following gases: (a) hydrogen, (b) helium, and (c) carbon monoxide.
- An inflated rubber balloon filled with air is immersed in a flask of liquid nitrogen that is at 77 K. Describe what happens to the balloon, assuming that it remains flexible while being cooled.
- Two identical cylinders at the same temperature each contain the same kind of gas and the same number of moles of gas. If the volume of cylinder A is three times greater than the volume of cylinder B, what can you say about the relative pressures in the cylinders?
- The pendulum of a certain pendulum clock is made of brass. When the temperature increases, does the clock run too fast, run too slowly, or remain unchanged? Explain.
- An automobile radiator is filled to the brim with water while the engine is cool. What happens to the water when the engine is running and the water is heated? What do modern automobiles have in their cooling systems to prevent the loss of coolants?
- Metal lids on glass jars can often be loosened by running them under hot water. How is this possible?
- When the metal ring and metal sphere shown in Figure Q19.15 are both at room temperature, the sphere can just be passed through the ring. After the sphere is heated, it cannot be passed through the ring. Explain.



Figure Q19.15 (Courtesy of Central Scientific Company)

PROBLEMS

1, 2, 3 = straightforward, intermediate, challenging □ = full solution available in the *Student Solutions Manual and Study Guide*

WEB = solution posted at <http://www.saunderscollege.com/physics/> = Computer useful in solving problem = Interactive Physics

= paired numerical/symbolic problems

Section 19.1 Temperature and the Zeroth Law of Thermodynamics

Section 19.2 Thermometers and the Celsius Temperature Scale

Section 19.3 The Constant-Volume Gas Thermometer and the Absolute Temperature Scale

Note: A pressure of 1 atm = 1.013×10^5 Pa = 101.3 kPa.

- Convert the following to equivalent temperatures on the Celsius and Kelvin scales: (a) the normal human

body temperature, 98.6°F; (b) the air temperature on a cold day, -5.00°F .

- In a constant-volume gas thermometer, the pressure at 20.0°C is 0.980 atm. (a) What is the pressure at 45.0°C ? (b) What is the temperature if the pressure is 0.500 atm?

WEB 3. A constant-volume gas thermometer is calibrated in dry ice (that is, carbon dioxide in the solid state, which has a temperature of -80.0°C) and in boiling ethyl alcohol (78.0°C). The two pressures are 0.900 atm and

- 1.635 atm. (a) What Celsius value of absolute zero does the calibration yield? What is the pressure at (b) the freezing point of water and (c) the boiling point of water?
- There is a temperature whose numerical value is the same on both the Celsius and Fahrenheit scales. What is this temperature?
 - Liquid nitrogen has a boiling point of -195.81°C at atmospheric pressure. Express this temperature in (a) degrees Fahrenheit and (b) kelvins.
 - On a Strange temperature scale, the freezing point of water is -15.0°S and the boiling point is $+60.0^{\circ}\text{S}$. Develop a *linear* conversion equation between this temperature scale and the Celsius scale.
 - The temperature difference between the inside and the outside of an automobile engine is 450°C . Express this temperature difference on the (a) Fahrenheit scale and (b) Kelvin scale.
 - The melting point of gold is $1\,064^{\circ}\text{C}$, and the boiling point is $2\,660^{\circ}\text{C}$. (a) Express these temperatures in kelvins. (b) Compute the difference between these temperatures in Celsius degrees and in kelvins.

Section 19.4 Thermal Expansion of Solids and Liquids

Note: When solving the problems in this section, use the data in Table 19.2.

- A copper telephone wire has essentially no sag between poles 35.0 m apart on a winter day when the temperature is -20.0°C . How much longer is the wire on a summer day when $T_{\text{C}} = 35.0^{\circ}\text{C}$?
- The concrete sections of a certain superhighway are designed to have a length of 25.0 m. The sections are poured and cured at 10.0°C . What minimum spacing should the engineer leave between the sections to eliminate buckling if the concrete is to reach a temperature of 50.0°C ?
- An aluminum tube is 3.000 0 m long at 20.0°C . What is its length at (a) 100.0°C and (b) 0.0°C ?
- A brass ring with a diameter of 10.00 cm at 20.0°C is heated and slipped over an aluminum rod with a diameter of 10.01 cm at 20.0°C . Assume that the average coefficients of linear expansion are constant. (a) To what temperature must this combination be cooled to separate them? Is this temperature attainable? (b) If the aluminum rod were 10.02 cm in diameter, what would be the required temperature?
- A pair of eyeglass frames is made of epoxy plastic. At room temperature (20.0°C), the frames have circular lens holes 2.20 cm in radius. To what temperature must the frames be heated if lenses 2.21 cm in radius are to be inserted in them? The average coefficient of linear expansion for epoxy is $1.30 \times 10^{-4} (^{\circ}\text{C})^{-1}$.
- The New River Gorge bridge in West Virginia is a steel arch bridge 518 m in length. How much does its length change between temperature extremes of -20.0°C and 35.0°C ?
- A square hole measuring 8.00 cm along each side is cut

in a sheet of copper. (a) Calculate the change in the area of this hole if the temperature of the sheet is increased by 50.0 K. (b) Does the result represent an increase or a decrease in the area of the hole?

- The average coefficient of volume expansion for carbon tetrachloride is $5.81 \times 10^{-4} (^{\circ}\text{C})^{-1}$. If a 50.0-gal steel container is filled completely with carbon tetrachloride when the temperature is 10.0°C , how much will spill over when the temperature rises to 30.0°C ?
- WEB** The active element of a certain laser is a glass rod 30.0 cm long by 1.50 cm in diameter. If the temperature of the rod increases by 65.0°C , what is the increase in (a) its length, (b) its diameter, and (c) its volume? (Assume that $\alpha = 9.00 \times 10^{-6} (^{\circ}\text{C})^{-1}$.)
- A volumetric glass flask made of Pyrex is calibrated at 20.0°C . It is filled to the 100-mL mark with 35.0°C acetone with which it immediately comes to thermal equilibrium. (a) What is the volume of the acetone when it cools to 20.0°C ? (b) How significant is the change in volume of the flask?
- A concrete walk is poured on a day when the temperature is 20.0°C , in such a way that the ends are unable to move. (a) What is the stress in the cement on a hot day of 50.0°C ? (b) Does the concrete fracture? Take Young's modulus for concrete to be $7.00 \times 10^9 \text{ N/m}^2$ and the tensile strength to be $2.00 \times 10^9 \text{ N/m}^2$.
- Figure P19.20 shows a circular steel casting with a gap. If the casting is heated, (a) does the width of the gap increase or decrease? (b) The gap width is 1.600 cm when the temperature is 30.0°C . Determine the gap width when the temperature is 190°C .

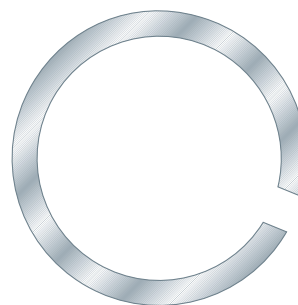


Figure P19.20

- A steel rod undergoes a stretching force of 500 N. Its cross-sectional area is 2.00 cm^2 . Find the change in temperature that would elongate the rod by the same amount that the 500-N force does. (*Hint:* Refer to Tables 12.1 and 19.2.)
- A steel rod 4.00 cm in diameter is heated so that its temperature increases by 70.0°C . It is then fastened between two rigid supports. The rod is allowed to cool to its original temperature. Assuming that Young's modulus for the steel is $20.6 \times 10^{10} \text{ N/m}^2$ and that its average

coefficient of linear expansion is $11.0 \times 10^{-6} (\text{°C})^{-1}$, calculate the tension in the rod.

23. A hollow aluminum cylinder 20.0 cm deep has an internal capacity of 2.000 L at 20.0°C. It is completely filled with turpentine and then warmed to 80.0°C. (a) How much turpentine overflows? (b) If the cylinder is then cooled back to 20.0°C, how far below the surface of the cylinder's rim does the turpentine's surface recede?
24. At 20.0°C, an aluminum ring has an inner diameter of 5.000 0 cm and a brass rod has a diameter of 5.050 0 cm. (a) To what temperature must the ring be heated so that it will just slip over the rod? (b) To what common temperature must the two be heated so that the ring just slips over the rod? Would this latter process work?

Section 19.5 Macroscopic Description of an Ideal Gas

25. Gas is contained in an 8.00-L vessel at a temperature of 20.0°C and a pressure of 9.00 atm. (a) Determine the number of moles of gas in the vessel. (b) How many molecules of gas are in the vessel?
26. A tank having a volume of 0.100 m³ contains helium gas at 150 atm. How many balloons can the tank blow up if each filled balloon is a sphere 0.300 m in diameter at an absolute pressure of 1.20 atm?
27. An auditorium has dimensions 10.0 m \times 20.0 m \times 30.0 m. How many molecules of air fill the auditorium at 20.0°C and a pressure of 101 kPa?
28. Nine grams of water are placed in a 2.00-L pressure cooker and heated to 500°C. What is the pressure inside the container if no gas escapes?
- WEB 29. The mass of a hot-air balloon and its cargo (not including the air inside) is 200 kg. The air outside is at 10.0°C and 101 kPa. The volume of the balloon is 400 m³. To what temperature must the air in the balloon be heated before the balloon will lift off? (Air density at 10.0°C is 1.25 kg/m³.)
30. One mole of oxygen gas is at a pressure of 6.00 atm and a temperature of 27.0°C. (a) If the gas is heated at constant volume until the pressure triples, what is the final temperature? (b) If the gas is heated until both the pressure and the volume are doubled, what is the final temperature?
31. (a) Find the number of moles in 1.00 m³ of an ideal gas at 20.0°C and atmospheric pressure. (b) For air, Avogadro's number of molecules has a mass of 28.9 g. Calculate the mass of 1 m³ of air. Compare the result with the tabulated density of air.
32. A cube 10.0 cm on each edge contains air (with equivalent molar mass 28.9 g/mol) at atmospheric pressure and temperature 300 K. Find (a) the mass of the gas, (b) its weight, and (c) the force it exerts on each face of the cube. (d) Comment on the underlying physical reason why such a small sample can exert such a great force.
33. An automobile tire is inflated with air originally at 10.0°C and normal atmospheric pressure. During the

process, the air is compressed to 28.0% of its original volume and its temperature is increased to 40.0°C.

- (a) What is the tire pressure? (b) After the car is driven at high speed, the tire air temperature rises to 85.0°C and the interior volume of the tire increases by 2.00%. What is the new tire pressure (absolute) in pascals?
34. A spherical weather balloon is designed to expand to a maximum radius of 20.0 m when in flight at its working altitude, where the air pressure is 0.030 0 atm and the temperature is 200 K. If the balloon is filled at atmospheric pressure and 300 K, what is its radius at liftoff?
35. A room of volume 80.0 m³ contains air having an equivalent molar mass of 28.9 g/mol. If the temperature of the room is raised from 18.0°C to 25.0°C, what mass of air (in kilograms) will leave the room? Assume that the air pressure in the room is maintained at 101 kPa.
36. A room of volume V contains air having equivalent molar mass M (in g/mol). If the temperature of the room is raised from T_1 to T_2 , what mass of air will leave the room? Assume that the air pressure in the room is maintained at P_0 .
37. At 25.0 m below the surface of the sea (density = 1 025 kg/m³), where the temperature is 5.00°C, a diver exhales an air bubble having a volume of 1.00 cm³. If the surface temperature of the sea is 20.0°C, what is the volume of the bubble right before it breaks the surface?
38. Estimate the mass of the air in your bedroom. State the quantities you take as data and the value you measure or estimate for each.
39. The pressure gauge on a tank registers the gauge pressure, which is the difference between the interior and exterior pressures. When the tank is full of oxygen (O₂), it contains 12.0 kg of the gas at a gauge pressure of 40.0 atm. Determine the mass of oxygen that has been withdrawn from the tank when the pressure reading is 25.0 atm. Assume that the temperature of the tank remains constant.
40. In state-of-the-art vacuum systems, pressures as low as 10^{-9} Pa are being attained. Calculate the number of molecules in a 1.00-m³ vessel at this pressure if the temperature is 27°C.
41. Show that 1 mol of any gas (assumed to be ideal) at atmospheric pressure (101.3 kPa) and standard temperature (273 K) occupies a volume of 22.4 L.
42. A diving bell in the shape of a cylinder with a height of 2.50 m is closed at the upper end and open at the lower end. The bell is lowered from air into sea water ($\rho = 1.025 \text{ g/cm}^3$). The air in the bell is initially at 20.0°C. The bell is lowered to a depth (measured to the bottom of the bell) of 45.0 fathoms, or 82.3 m. At this depth, the water temperature is 4.0°C, and the air in the bell is in thermal equilibrium with the water. (a) How high does sea water rise in the bell? (b) To what minimum pressure must the air in the bell be increased for the water that entered to be expelled?

ADDITIONAL PROBLEMS

43. A student measures the length of a brass rod with a steel tape at 20.0°C . The reading is 95.00 cm. What will the tape indicate for the length of the rod when the rod and the tape are at (a) -15.0°C and (b) 55.0°C ?
44. The density of gasoline is 730 kg/m^3 at 0°C . Its average coefficient of volume expansion is $9.60 \times 10^{-4} (^\circ\text{C})^{-1}$. If 1.00 gal of gasoline occupies 0.00380 m^3 , how many extra kilograms of gasoline would you get if you bought 10.0 gal of gasoline at 0°C rather than at 20.0°C from a pump that is not temperature compensated?
45. A steel ball bearing is 4.000 cm in diameter at 20.0°C . A bronze plate has a hole in it that is 3.994 cm in diameter at 20.0°C . What common temperature must they have so that the ball just squeezes through the hole?
46. **Review Problem.** An aluminum pipe 0.655 m long at 20.0°C and open at both ends is used as a flute. The pipe is cooled to a low temperature but is then filled with air at 20.0°C as soon as it is played. By how much does its fundamental frequency change as the temperature of the metal increases from 5.00°C to 20.0°C ?
47. A mercury thermometer is constructed as shown in Figure P19.47. The capillary tube has a diameter of 0.00400 cm, and the bulb has a diameter of 0.250 cm. Neglecting the expansion of the glass, find the change in height of the mercury column that occurs with a temperature change of 30.0°C .

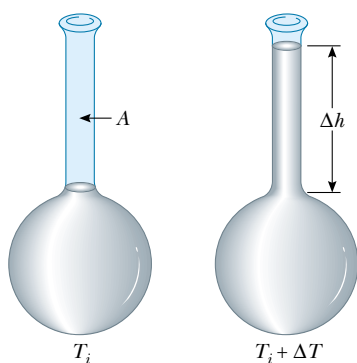


Figure P19.47 Problems 47 and 48.

48. A liquid with a coefficient of volume expansion β just fills a spherical shell of volume V_i at a temperature of T_i (see Fig. P19.47). The shell is made of a material that has an average coefficient of linear expansion α . The liquid is free to expand into an open capillary of area A projecting from the top of the sphere. (a) If the temperature increases by ΔT , show that the liquid rises in the capillary by the amount Δh given by the equation $\Delta h = (V_i/A)(\beta - 3\alpha)\Delta T$. (b) For a typical system, such as a mercury thermometer, why is it a good approximation to neglect the expansion of the shell?

- WEB 49. A liquid has a density ρ . (a) Show that the fractional change in density for a change in temperature ΔT is $\Delta\rho/\rho = -\beta\Delta T$. What does the negative sign signify? (b) Fresh water has a maximum density of 1.0000 g/cm^3 at 4.0°C . At 10.0°C , its density is 0.9997 g/cm^3 . What is β for water over this temperature interval?
50. A cylinder is closed by a piston connected to a spring of constant $2.00 \times 10^3\text{ N/m}$ (Fig. P19.50). While the spring is relaxed, the cylinder is filled with 5.00 L of gas at a pressure of 1.00 atm and a temperature of 20.0°C . (a) If the piston has a cross-sectional area of 0.0100 m^2 and a negligible mass, how high will it rise when the temperature is increased to 250°C ? (b) What is the pressure of the gas at 250°C ?

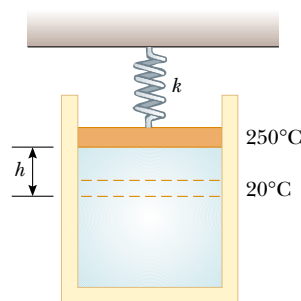


Figure P19.50

- WEB 51. A vertical cylinder of cross-sectional area A is fitted with a tight-fitting, frictionless piston of mass m (Fig. P19.51). (a) If n moles of an ideal gas are in the cylinder at a temperature of T , what is the height h at which the piston is in equilibrium under its own weight? (b) What is the value for h if $n = 0.200\text{ mol}$, $T = 400\text{ K}$, $A = 0.00800\text{ m}^2$, and $m = 20.0\text{ kg}$?

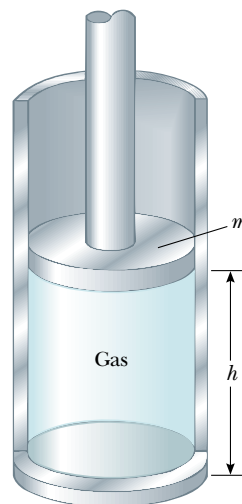


Figure P19.51

52. A bimetallic bar is made of two thin strips of dissimilar metals bonded together. As they are heated, the one with the greater average coefficient of expansion expands more than the other, forcing the bar into an arc, with the outer radius having a greater circumference (Fig. P19.52). (a) Derive an expression for the angle of bending θ as a function of the initial length of the strips, their average coefficients of linear expansion, the change in temperature, and the separation of the centers of the strips ($\Delta r = r_2 - r_1$). (b) Show that the angle of bending decreases to zero when ΔT decreases to zero or when the two average coefficients of expansion become equal. (c) What happens if the bar is cooled?

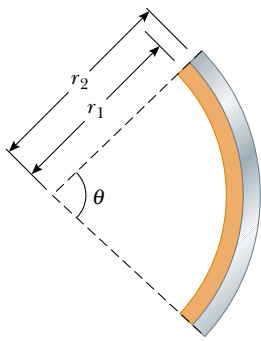


Figure P19.52

53. The rectangular plate shown in Figure P19.53 has an area A_i equal to ℓw . If the temperature increases by ΔT , show that the increase in area is $\Delta A = 2\alpha A_i \Delta T$, where α is the average coefficient of linear expansion. What approximation does this expression assume? (Hint: Note that each dimension increases according to the equation $\Delta L = \alpha L_i \Delta T$.)

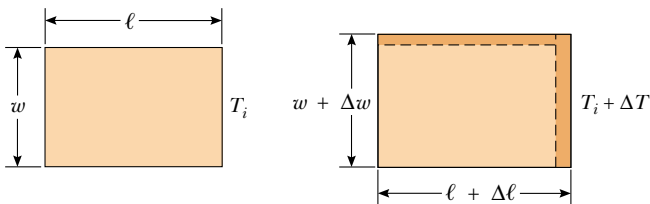


Figure P19.53

54. Precise temperature measurements are often made on the basis of the change in electrical resistance of a metal with temperature. The resistance varies approximately according to the expression $R = R_0(1 + AT_C)$, where R_0 and A are constants. A certain element has a resistance of 50.0 ohms (Ω) at 0°C and 71.5Ω at the freezing point of tin (231.97°C). (a) Determine the constants A and R_0 . (b) At what temperature is the resistance equal to 89.0Ω ?

55. **Review Problem.** A clock with a brass pendulum has a period of 1.000 s at 20.0°C . If the temperature increases to 30.0°C , (a) by how much does the period change, and (b) how much time does the clock gain or lose in one week?
56. **Review Problem.** Consider an object with any one of the shapes displayed in Table 10.2. What is the percentage increase in the moment of inertia of the object when it is heated from 0°C to 100°C if it is composed of (a) copper or (b) aluminum? (See Table 19.2. Assume that the average linear expansion coefficients do not vary between 0°C and 100°C .)
57. **Review Problem.** (a) Derive an expression for the buoyant force on a spherical balloon that is submerged in water as a function of the depth below the surface, the volume (V_i) of the balloon at the surface, the pressure (P_0) at the surface, and the density of the water. (Assume that water temperature does not change with depth.) (b) Does the buoyant force increase or decrease as the balloon is submerged? (c) At what depth is the buoyant force one-half the surface value?
58. (a) Show that the density of an ideal gas occupying a volume V is given by $\rho = PM/RT$, where M is the molar mass. (b) Determine the density of oxygen gas at atmospheric pressure and 20.0°C .
59. Starting with Equation 19.10, show that the total pressure P in a container filled with a mixture of several ideal gases is $P = P_1 + P_2 + P_3 + \dots$, where P_1 , P_2 , \dots are the pressures that each gas would exert if it alone filled the container. (These individual pressures are called the *partial pressures* of the respective gases.) This is known as *Dalton's law of partial pressures*.
60. A sample of dry air that has a mass of 100.00 g, collected at sea level, is analyzed and found to consist of the following gases:

nitrogen (N_2) = 75.52 g

oxygen (O_2) = 23.15 g

argon (Ar) = 1.28 g

carbon dioxide (CO_2) = 0.05 g

as well as trace amounts of neon, helium, methane, and other gases. (a) Calculate the partial pressure (see Problem 59) of each gas when the pressure is 101.3 kPa.

(b) Determine the volume occupied by the 100-g sample at a temperature of 15.00°C and a pressure of $1.013 \times 10^5 \text{ Pa}$. What is the density of the air for these conditions? (c) What is the effective molar mass of the air sample?

61. Steel rails for an interurban rapid transit system form a continuous track that is held rigidly in place in concrete. (a) If the track was laid when the temperature was 0°C , what is the stress in the rails on a warm day when the temperature is 25.0°C ? (b) What fraction of the yield strength of $52.2 \times 10^7 \text{ N/m}^2$ does this stress represent?

62. (a) Use the equation of state for an ideal gas and the definition of the average coefficient of volume expansion, in the form $\beta = (1/V)dV/dT$, to show that the average coefficient of volume expansion for an ideal gas at constant pressure is given by $\beta = 1/T$, where T is the absolute temperature. (b) What value does this expression predict for β at 0°C ? Compare this with the experimental values for helium and air in Table 19.2.
63. Two concrete spans of a 250-m-long bridge are placed end to end so that no room is allowed for expansion (Fig. P19.63a). If a temperature increase of 20.0°C occurs, what is the height y to which the spans rise when they buckle (Fig. P19.63b)?
64. Two concrete spans of a bridge of length L are placed end to end so that no room is allowed for expansion (see Fig. P19.63a). If a temperature increase of ΔT occurs, what is the height y to which the spans rise when they buckle (see Fig. P19.63b)?

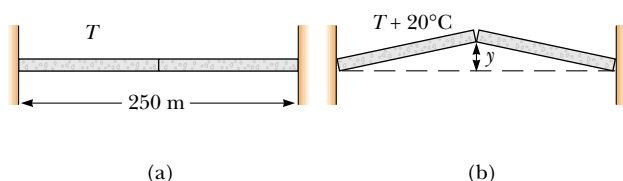


Figure P19.63 Problems 63 and 64.

65. A copper rod and a steel rod are heated. At 0°C the copper rod has length L_c and the steel rod has length L_s . When the rods are being heated or cooled, the difference between their lengths stays constant at 5.00 cm. Determine the values of L_c and L_s .
66. A cylinder that has a 40.0-cm radius and is 50.0 cm deep is filled with air at 20.0°C and 1.00 atm (Fig. P19.66a). A 20.0-kg piston is now lowered into the cylinder, compressing the air trapped inside (Fig. P19.66b). Finally, a 75.0-kg man stands on the piston, further compressing the air, which remains at 20°C (Fig. P19.66c). (a) How far down (Δh) does the piston move when the man steps onto it? (b) To what temperature should the gas be heated to raise the piston and the man back to h_i ?
67. The relationship $L_f = L_i(1 + \alpha\Delta T)$ is an approximation that works when the average coefficient of expansion is small. If α is large, one must integrate the relationship $dL/dT = \alpha L$ to determine the final length. (a) Assuming that the average coefficient of linear expansion is constant as L varies, determine a general expression for the final length. (b) Given a rod of length 1.00 m and a temperature change of 100.0°C , determine the error caused by the approximation when $\alpha = 2.00 \times 10^{-5} (^\circ\text{C})^{-1}$ (a typical value for a metal) and

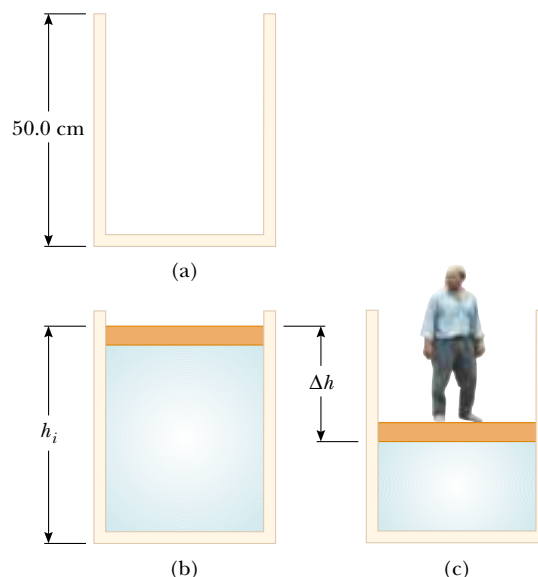


Figure P19.66

when $\alpha = 0.0200 (^\circ\text{C})^{-1}$ (an unrealistically large value for comparison).

68. A steel wire and a copper wire, each of diameter 2.000 mm, are joined end to end. At 40.0°C , each has an unstretched length of 2.000 m; they are connected between two fixed supports 4.000 m apart on a tabletop, so that the steel wire extends from $x = -2.000$ m to $x = 0$, the copper wire extends from $x = 0$ to $x = 2.000$ m, and the tension is negligible. The temperature is then lowered to 20.0°C . At this lower temperature, what are the tension in the wire and the x coordinate of the junction between the wires? (Refer to Tables 12.1 and 19.2.)
69. **Review Problem.** A steel guitar string with a diameter of 1.00 mm is stretched between supports 80.0 cm apart. The temperature is 0.0°C . (a) Find the mass per unit length of this string. (Use $7.86 \times 10^3 \text{ kg/m}^3$ as the mass density.) (b) The fundamental frequency of transverse oscillations of the string is 200 Hz. What is the tension in the string? (c) If the temperature is raised to 30.0°C , find the resulting values of the tension and the fundamental frequency. (Assume that both the Young's modulus [Table 12.1] and the average coefficient of linear expansion [Table 19.2] have constant values between 0.0°C and 30.0°C .)
70. A 1.00-km steel railroad rail is fastened securely at both ends when the temperature is 20.0°C . As the temperature increases, the rail begins to buckle. If its shape is an arc of a vertical circle, find the height h of the center of the buckle when the temperature is 25.0°C . (You will need to solve a transcendental equation.)

ANSWERS TO QUICK QUIZZES

- 19.1** The size of a degree on the Fahrenheit scale is $\frac{5}{9}$ the size of a degree on the Celsius scale. This is true because the Fahrenheit range of 32°F to 212°F is equivalent to the Celsius range of 0°C to 100°C. The factor $\frac{9}{5}$ in Equation 19.2 corrects for this difference. Equation 19.1 does not need this correction because the size of a Celsius degree is the same as the size of a kelvin.
- 19.2** The glass bulb containing most of the mercury warms up first because it is in direct thermal contact with the hot water. It expands slightly, and thus its volume increases. This causes the mercury level in the capillary tube to drop. As the mercury inside the bulb warms up, it also expands. Eventually, its increase in volume is sufficient to raise the mercury level in the capillary tube.
- 19.3** For the glass, choose Pyrex, which has a lower average coefficient of linear expansion than does ordinary glass. For the working liquid, choose gasoline, which has the largest average coefficient of volume expansion.
- 19.4** You do not have to convert the units for pressure and volume to SI units as long as the same units appear in the numerator and the denominator. This is not true for ratios of temperature units, as you can see by comparing the ratios 300 K/200 K and 26.85°C/(−73.15°C). You must always use absolute (kelvin) temperatures when applying the ideal gas law.

PUZZLER

Biting into a hot piece of pizza can be either a pleasant experience or a painful one, depending on how it is done. Eating the crust doesn't usually cause a problem, but if you get a mouthful of hot cheese, you can be left with a burned palate. Why does it make so much difference whether your mouth touches the crust or the cheese when both are at the same temperature? (Charles D. Winters)



chapter

20

Heat and the First Law of Thermodynamics

Chapter Outline

- | | |
|--|--|
| 20.1 Heat and Internal Energy | 20.5 The First Law of Thermodynamics |
| 20.2 Heat Capacity and Specific Heat | 20.6 Some Applications of the First Law of Thermodynamics |
| 20.3 Latent Heat | 20.7 Energy Transfer Mechanisms |
| 20.4 Work and Heat in Thermodynamic Processes | |

Until about 1850, the fields of thermodynamics and mechanics were considered two distinct branches of science, and the law of conservation of energy seemed to describe only certain kinds of mechanical systems. However, mid-19th century experiments performed by the Englishman James Joule and others showed that energy may be added to (or removed from) a system either by heat or by doing work on the system (or having the system do work). Today we know that internal energy, which we formally define in this chapter, can be transformed to mechanical energy. Once the concept of energy was broadened to include internal energy, the law of conservation of energy emerged as a universal law of nature.

This chapter focuses on the concept of internal energy, the processes by which energy is transferred, the first law of thermodynamics, and some of the important applications of the first law. The first law of thermodynamics is the law of conservation of energy. It describes systems in which the only energy change is that of internal energy, which is due to transfers of energy by heat or work. Furthermore, the first law makes no distinction between the results of heat and the results of work. According to the first law, a system's internal energy can be changed either by an energy transfer by heat to or from the system or by work done on or by the system.

20.1 HEAT AND INTERNAL ENERGY

10.3 At the outset, it is important that we make a major distinction between internal energy and heat. **Internal energy is all the energy of a system that is associated with its microscopic components—atoms and molecules—when viewed from a reference frame at rest with respect to the object.** The last part of this sentence ensures that any bulk kinetic energy of the system due to its motion through space is not included in internal energy. Internal energy includes kinetic energy of translation, rotation, and vibration of molecules, potential energy within molecules, and potential energy between molecules. It is useful to relate internal energy to the temperature of an object, but this relationship is limited—we shall find in Section 20.3 that internal energy changes can also occur in the absence of temperature changes.

As we shall see in Chapter 21, the internal energy of a monatomic ideal gas is associated with the translational motion of its atoms. This is the only type of energy available for the microscopic components of this system. In this special case, the internal energy is simply the total kinetic energy of the atoms of the gas; the higher the temperature of the gas, the greater the average kinetic energy of the atoms and the greater the internal energy of the gas. More generally, in solids, liquids, and molecular gases, internal energy includes other forms of molecular energy. For example, a diatomic molecule can have rotational kinetic energy, as well as vibrational kinetic and potential energy.

Heat is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings. When you *heat* a substance, you are transferring energy into it by placing it in contact with surroundings that have a higher temperature. This is the case, for example, when you place a pan of cold water on a stove burner—the burner is at a higher temperature than the water, and so the water gains energy. We shall also use the term *heat* to represent the amount of energy transferred by this method.

Scientists used to think of heat as a fluid called *caloric*, which they believed was transferred between objects; thus, they defined heat in terms of the temperature changes produced in an object during heating. Today we recognize the distinct difference between internal energy and heat. Nevertheless, we refer to quantities



James Prescott Joule British physicist (1818–1889) Joule received some formal education in mathematics, philosophy, and chemistry but was in large part self-educated. His research led to the establishment of the principle of conservation of energy. His study of the quantitative relationship among electrical, mechanical, and chemical effects of heat culminated in his discovery in 1843 of the amount of work required to produce a unit of energy, called the mechanical equivalent of heat. (By kind permission of the President and Council of the Royal Society)

Heat

using names that do not quite correctly define the quantities but which have become entrenched in physics tradition based on these early ideas. Examples of such quantities are *latent heat* and *heat capacity*.

As an analogy to the distinction between heat and internal energy, consider the distinction between work and mechanical energy discussed in Chapter 7. The work done on a system is a measure of the amount of energy transferred to the system from its surroundings, whereas the mechanical energy of the system (kinetic or potential, or both) is a consequence of the motion and relative positions of the members of the system. Thus, when a person does work on a system, energy is transferred from the person to the system. It makes no sense to talk about the work *of* a system—one can refer only to the work done *on* or *by* a system when some process has occurred in which energy has been transferred to or from the system. Likewise, it makes no sense to talk about the heat *of* a system—one can refer to *heat* only when energy has been transferred as a result of a temperature difference. Both heat and work are ways of changing the energy of a system.

It is also important to recognize that the internal energy of a system can be changed even when no energy is transferred by heat. For example, when a gas is compressed by a piston, the gas is warmed and its internal energy increases, but no transfer of energy by heat from the surroundings to the gas has occurred. If the gas then expands rapidly, it cools and its internal energy decreases, but no transfer of energy by heat from it to the surroundings has taken place. The temperature changes in the gas are due not to a difference in temperature between the gas and its surroundings but rather to the compression and the expansion. In each case, energy is transferred to or from the gas by *work*, and the energy change within the system is an increase or decrease of internal energy. The changes in internal energy in these examples are evidenced by corresponding changes in the temperature of the gas.

Units of Heat

As we have mentioned, early studies of heat focused on the resultant increase in temperature of a substance, which was often water. The early notions of heat based on caloric suggested that the flow of this fluid from one body to another caused changes in temperature. From the name of this mythical fluid, we have an energy unit related to thermal processes, the **calorie (cal)**, which is defined as **the amount of energy transfer necessary to raise the temperature of 1 g of water from 14.5°C to 15.5°C.**¹ (Note that the “Calorie,” written with a capital “C” and used in describing the energy content of foods, is actually a kilocalorie.) The unit of energy in the British system is the **British thermal unit (Btu)**, which is defined as **the amount of energy transfer required to raise the temperature of 1 lb of water from 63°F to 64°F.**

Scientists are increasingly using the SI unit of energy, the *joule*, when describing thermal processes. In this textbook, heat and internal energy are usually measured in joules. (Note that both heat and work are measured in energy units. Do not confuse these two means of energy *transfer* with energy itself, which is also measured in joules.)

¹ Originally, the calorie was defined as the “heat” necessary to raise the temperature of 1 g of water by 1°C. However, careful measurements showed that the amount of energy required to produce a 1°C change depends somewhat on the initial temperature; hence, a more precise definition evolved.

The Mechanical Equivalent of Heat

In Chapters 7 and 8, we found that whenever friction is present in a mechanical system, some mechanical energy is lost—in other words, mechanical energy is not conserved in the presence of nonconservative forces. Various experiments show that this lost mechanical energy does not simply disappear but is transformed into internal energy. We can perform such an experiment at home by simply hammering a nail into a scrap piece of wood. What happens to all the kinetic energy of the hammer once we have finished? Some of it is now in the nail as internal energy, as demonstrated by the fact that the nail is measurably warmer. Although this connection between mechanical and internal energy was first suggested by Benjamin Thompson, it was Joule who established the equivalence of these two forms of energy.

A schematic diagram of Joule's most famous experiment is shown in Figure 20.1. The system of interest is the water in a thermally insulated container. Work is done on the water by a rotating paddle wheel, which is driven by heavy blocks falling at a constant speed. The stirred water is warmed due to the friction between it and the paddles. If the energy lost in the bearings and through the walls is neglected, then the loss in potential energy associated with the blocks equals the work done by the paddle wheel on the water. If the two blocks fall through a distance h , the loss in potential energy is $2mgh$, where m is the mass of one block; it is this energy that causes the temperature of the water to increase. By varying the conditions of the experiment, Joule found that the loss in mechanical energy $2mgh$ is proportional to the increase in water temperature ΔT . The proportionality constant was found to be approximately $4.18 \text{ J/g} \cdot ^\circ\text{C}$. Hence, 4.18 J of mechanical energy raises the temperature of 1 g of water by 1°C . More precise measurements taken later demonstrated the proportionality to be $4.186 \text{ J/g} \cdot ^\circ\text{C}$ when the temperature of the water was raised from 14.5°C to 15.5°C . We adopt this “15-degree calorie” value:

$$1 \text{ cal} \equiv 4.186 \text{ J} \quad (20.1)$$

This equality is known, for purely historical reasons, as the **mechanical equivalent of heat**.



Benjamin Thompson
(1753–1814).

Mechanical equivalent of heat

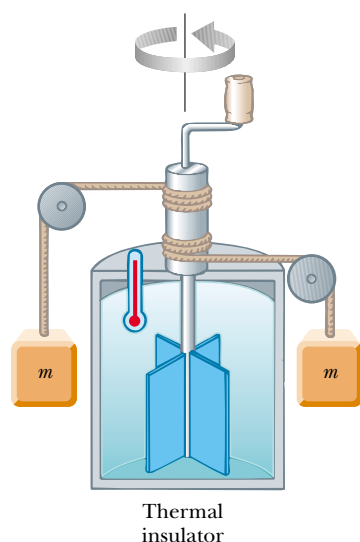


Figure 20.1 Joule's experiment for determining the mechanical equivalent of heat. The falling blocks rotate the paddles, causing the temperature of the water to increase.

EXAMPLE 20.1 Losing Weight the Hard Way

A student eats a dinner rated at 2 000 Calories. He wishes to do an equivalent amount of work in the gymnasium by lifting a 50.0-kg barbell. How many times must he raise the barbell to expend this much energy? Assume that he raises the barbell 2.00 m each time he lifts it and that he regains no energy when he drops the barbell to the floor.

Solution Because 1 Calorie = 1.00×10^3 cal, the work required is 2.00×10^6 cal. Converting this value to joules, we have for the total work required:

$$W = (2.00 \times 10^6 \text{ cal})(4.186 \text{ J/cal}) = 8.37 \times 10^6 \text{ J}$$

The work done in lifting the barbell a distance h is equal to mgh , and the work done in lifting it n times is $nmg h$. We equate this to the total work required:

$$W = nmgh = 8.37 \times 10^6 \text{ J}$$

$$n = \frac{8.37 \times 10^6 \text{ J}}{(50.0 \text{ kg})(9.80 \text{ m/s}^2)(2.00 \text{ m})} = 8.54 \times 10^3 \text{ times}$$

If the student is in good shape and lifts the barbell once every 5 s, it will take him about 12 h to perform this feat. Clearly, it is much easier for this student to lose weight by dieting.

20.2 HEAT CAPACITY AND SPECIFIC HEAT

When energy is added to a substance and no work is done, the temperature of the substance usually rises. (An exception to this statement is the case in which a substance undergoes a change of state—also called a *phase transition*—as discussed in the next section.) The quantity of energy required to raise the temperature of a given mass of a substance by some amount varies from one substance to another. For example, the quantity of energy required to raise the temperature of 1 kg of water by 1°C is 4 186 J, but the quantity of energy required to raise the temperature of 1 kg of copper by 1°C is only 387 J. In the discussion that follows, we shall use heat as our example of energy transfer, but we shall keep in mind that we could change the temperature of our system by doing work on it.

The **heat capacity** C of a particular sample of a substance is defined as the amount of energy needed to raise the temperature of that sample by 1°C . From this definition, we see that if heat Q produces a change ΔT in the temperature of a substance, then

$$Q = C\Delta T \quad (20.2)$$

The **specific heat** c of a substance is the heat capacity per unit mass. Thus, if energy Q transferred by heat to mass m of a substance changes the temperature of the sample by ΔT , then the specific heat of the substance is

$$c \equiv \frac{Q}{m\Delta T} \quad (20.3)$$

Specific heat is essentially a measure of how thermally insensitive a substance is to the addition of energy. The greater a material's specific heat, the more energy must be added to a given mass of the material to cause a particular temperature change. Table 20.1 lists representative specific heats.

From this definition, we can express the energy Q transferred by heat between a sample of mass m of a material and its surroundings for a temperature change ΔT as

$$Q = mc\Delta T \quad (20.4)$$

For example, the energy required to raise the temperature of 0.500 kg of water by 3.00°C is $(0.500 \text{ kg})(4 186 \text{ J/kg} \cdot ^\circ\text{C})(3.00^\circ\text{C}) = 6.28 \times 10^3 \text{ J}$. Note that when the temperature increases, Q and ΔT are taken to be positive, and energy flows into

Heat capacity

Specific heat

TABLE 20.1 Specific Heats of Some Substances at 25°C and Atmospheric Pressure

Substance	Specific Heat c	
	J/kg · °C	cal/g · °C
Elemental Solids		
Aluminum	900	0.215
Beryllium	1 830	0.436
Cadmium	230	0.055
Copper	387	0.092 4
Germanium	322	0.077
Gold	129	0.030 8
Iron	448	0.107
Lead	128	0.030 5
Silicon	703	0.168
Silver	234	0.056
Other Solids		
Brass	380	0.092
Glass	837	0.200
Ice (− 5°C)	2 090	0.50
Marble	860	0.21
Wood	1 700	0.41
Liquids		
Alcohol (ethyl)	2 400	0.58
Mercury	140	0.033
Water (15°C)	4 186	1.00
Gas		
Steam (100°C)	2 010	0.48

the system. When the temperature decreases, Q and ΔT are negative, and energy flows out of the system.

Specific heat varies with temperature. However, if temperature intervals are not too great, the temperature variation can be ignored and c can be treated as a constant.² For example, the specific heat of water varies by only about 1% from 0°C to 100°C at atmospheric pressure. Unless stated otherwise, we shall neglect such variations.

Measured values of specific heats are found to depend on the conditions of the experiment. In general, measurements made at constant pressure are different from those made at constant volume. For solids and liquids, the difference between the two values is usually no greater than a few percent and is often neglected. Most of the values given in Table 20.1 were measured at atmospheric pressure and room temperature. As we shall see in Chapter 21, the specific heats for

² The definition given by Equation 20.3 assumes that the specific heat does not vary with temperature over the interval $\Delta T = T_f - T_i$. In general, if c varies with temperature over the interval, then the correct expression for Q is

$$Q = m \int_{T_i}^{T_f} c \, dT$$

gases measured at constant pressure are quite different from values measured at constant volume.

Quick Quiz 20.1

Imagine you have 1 kg each of iron, glass, and water, and that all three samples are at 10°C . (a) Rank the samples from lowest to highest temperature after 100 J of energy is added to each. (b) Rank them from least to greatest amount of energy transferred by heat if each increases in temperature by 20°C .

QuickLab

In an open area, such as a parking lot, use the flame from a match to pop an air-filled balloon. Now try the same thing with a water-filled balloon. Why doesn't the water-filled balloon pop?

It is interesting to note from Table 20.1 that water has the highest specific heat of common materials. This high specific heat is responsible, in part, for the moderate temperatures found near large bodies of water. As the temperature of a body of water decreases during the winter, energy is transferred from the cooling water to the air by heat, increasing the internal energy of the air. Because of the high specific heat of water, a relatively large amount of energy is transferred to the air for even modest temperature changes of the water. The air carries this internal energy landward when prevailing winds are favorable. For example, the prevailing winds on the West Coast of the United States are toward the land (eastward). Hence, the energy liberated by the Pacific Ocean as it cools keeps coastal areas much warmer than they would otherwise be. This explains why the western coastal states generally have more favorable winter weather than the eastern coastal states, where the prevailing winds do not tend to carry the energy toward land.



A difference in specific heats causes the cheese topping on a slice of pizza to burn you more than a mouthful of crust at the same temperature. Both crust and cheese undergo the same change in temperature, starting at a high straight-from-the-oven value and ending at the temperature of the inside of your mouth, which is about 37°C . Because the cheese is much more likely to burn you, it must release much more energy as it cools than does the crust. If we assume roughly the same mass for both cheese and crust, then Equation 20.3 indicates that the specific heat of the cheese, which is mostly water, is greater than that of the crust, which is mostly air.

Conservation of Energy: Calorimetry

One technique for measuring specific heat involves heating a sample to some known temperature T_x , placing it in a vessel containing water of known mass and temperature $T_w < T_x$, and measuring the temperature of the water after equilibrium has been reached. Because a negligible amount of mechanical work is done in the process, the law of the conservation of energy requires that the amount of energy that leaves the sample (of unknown specific heat) equal the amount of energy that enters the water.³ This technique is called **calorimetry**, and devices in which this energy transfer occurs are called **calorimeters**.

Conservation of energy allows us to write the equation

$$Q_{\text{cold}} = -Q_{\text{hot}} \quad (20.5)$$

which simply states that the energy leaving the hot part of the system by heat is equal to that entering the cold part of the system. The negative sign in the equation is necessary to maintain consistency with our sign convention for heat. The

³ For precise measurements, the water container should be included in our calculations because it also exchanges energy with the sample. However, doing so would require a knowledge of its mass and composition. If the mass of the water is much greater than that of the container, we can neglect the effects of the container.

heat Q_{hot} is negative because energy is leaving the hot sample. The negative sign in the equation ensures that the right-hand side is positive and thus consistent with the left-hand side, which is positive because energy is entering the cold water.

Suppose m_x is the mass of a sample of some substance whose specific heat we wish to determine. Let us call its specific heat c_x and its initial temperature T_x . Likewise, let m_w , c_w , and T_w represent corresponding values for the water. If T_f is the final equilibrium temperature after everything is mixed, then from Equation 20.4, we find that the energy transfer for the water is $m_w c_w (T_f - T_w)$, which is positive because $T_f > T_w$, and that the energy transfer for the sample of unknown specific heat is $m_x c_x (T_f - T_x)$, which is negative. Substituting these expressions into Equation 20.5 gives

$$m_w c_w (T_f - T_w) = -m_x c_x (T_f - T_x)$$

Solving for c_x gives

$$c_x = \frac{m_w c_w (T_f - T_w)}{m_x (T_x - T_f)}$$

EXAMPLE 20.2 Cooling a Hot Ingot

A 0.050 0-kg ingot of metal is heated to 200.0°C and then dropped into a beaker containing 0.400 kg of water initially at 20.0°C. If the final equilibrium temperature of the mixed system is 22.4°C, find the specific heat of the metal.

Solution According to Equation 20.5, we can write

$$\begin{aligned} m_w c_w (T_f - T_w) &= -m_x c_x (T_f - T_x) \\ (0.400 \text{ kg}) (4186 \text{ J/kg} \cdot ^\circ\text{C}) (22.4^\circ\text{C} - 20.0^\circ\text{C}) &= \\ &= -(0.050 0 \text{ kg}) (c_x) (22.4^\circ\text{C} - 200.0^\circ\text{C}) \end{aligned}$$

From this we find that

$$c_x = 453 \text{ J/kg} \cdot ^\circ\text{C}$$

The ingot is most likely iron, as we can see by comparing this result with the data given in Table 20.1. Note that the temperature of the ingot is initially above the steam point. Thus, some of the water may vaporize when we drop the ingot into the water. We assume that we have a sealed system and thus that this steam cannot escape. Because the final equilibrium temperature is lower than the steam point, any steam that does result recondenses back into water.

Exercise What is the amount of energy transferred to the water as the ingot is cooled?

Answer 4 020 J.

EXAMPLE 20.3 Fun Time for a Cowboy

A cowboy fires a silver bullet with a mass of 2.00 g and with a muzzle speed of 200 m/s into the pine wall of a saloon. Assume that all the internal energy generated by the impact remains with the bullet. What is the temperature change of the bullet?

Solution The kinetic energy of the bullet is

$$\frac{1}{2}mv^2 = \frac{1}{2}(2.00 \times 10^{-3} \text{ kg})(200 \text{ m/s})^2 = 40.0 \text{ J}$$

Because nothing in the environment is hotter than the bullet, the bullet gains no energy by heat. Its temperature increases because the 40.0 J of kinetic energy becomes 40.0 J of extra internal energy. The temperature change is the same as that which would take place if 40.0 J of energy were transferred by

heat from a stove to the bullet. If we imagine this latter process taking place, we can calculate ΔT from Equation 20.4. Using 234 J/kg·°C as the specific heat of silver (see Table 20.1), we obtain

$$\Delta T = \frac{Q}{mc} = \frac{40.0 \text{ J}}{(2.00 \times 10^{-3} \text{ kg})(234 \text{ J/kg} \cdot ^\circ\text{C})} = 85.5^\circ\text{C}$$

Exercise Suppose that the cowboy runs out of silver bullets and fires a lead bullet of the same mass and at the same speed into the wall. What is the temperature change of the bullet?

Answer 156°C.

20.3 LATENT HEAT

A substance often undergoes a change in temperature when energy is transferred between it and its surroundings. There are situations, however, in which the transfer of energy does not result in a change in temperature. This is the case whenever the physical characteristics of the substance change from one form to another; such a change is commonly referred to as a **phase change**. Two common phase changes are from solid to liquid (melting) and from liquid to gas (boiling); another is a change in the crystalline structure of a solid. All such phase changes involve a change in internal energy but no change in temperature. The increase in internal energy in boiling, for example, is represented by the breaking of bonds between molecules in the liquid state; this bond breaking allows the molecules to move farther apart in the gaseous state, with a corresponding increase in intermolecular potential energy.

As you might expect, different substances respond differently to the addition or removal of energy as they change phase because their internal molecular arrangements vary. Also, the amount of energy transferred during a phase change depends on the amount of substance involved. (It takes less energy to melt an ice cube than it does to thaw a frozen lake.) If a quantity Q of energy transfer is required to change the phase of a mass m of a substance, the ratio $L \equiv Q/m$ characterizes an important thermal property of that substance. Because this added or removed energy does not result in a temperature change, the quantity L is called the **latent heat** (literally, the “hidden” heat) of the substance. The value of L for a substance depends on the nature of the phase change, as well as on the properties of the substance.

From the definition of latent heat, and again choosing heat as our energy transfer mechanism, we find that the energy required to change the phase of a given mass m of a pure substance is

$$Q = mL \quad (20.6)$$

Latent heat of fusion L_f is the term used when the phase change is from solid to liquid (*to fuse* means “to combine by melting”), and **latent heat of vaporization**

TABLE 20.2 Latent Heats of Fusion and Vaporization

Substance	Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)
Helium	−269.65	5.23×10^3	−268.93	2.09×10^4
Nitrogen	−209.97	2.55×10^4	−195.81	2.01×10^5
Oxygen	−218.79	1.38×10^4	−182.97	2.13×10^5
Ethyl alcohol	−114	1.04×10^5	78	8.54×10^5
Water	0.00	3.33×10^5	100.00	2.26×10^6
Sulfur	119	3.81×10^4	444.60	3.26×10^5
Lead	327.3	2.45×10^4	1 750	8.70×10^5
Aluminum	660	3.97×10^5	2 450	1.14×10^7
Silver	960.80	8.82×10^4	2 193	2.33×10^6
Gold	1 063.00	6.44×10^4	2 660	1.58×10^6
Copper	1 083	1.34×10^5	1 187	5.06×10^6

L_v is the term used when the phase change is from liquid to gas (the liquid “vaporizes”).⁴ The latent heats of various substances vary considerably, as data in Table 20.2 show.

Quick Quiz 20.2

Which is more likely to cause a serious burn, 100°C liquid water or an equal mass of 100°C steam?

To understand the role of latent heat in phase changes, consider the energy required to convert a 1.00-g block of ice at -30.0°C to steam at 120.0°C . Figure 20.2 indicates the experimental results obtained when energy is gradually added to the ice. Let us examine each portion of the red curve.

Part A. On this portion of the curve, the temperature of the ice changes from -30.0°C to 0.0°C . Because the specific heat of ice is $2.090\text{ J/kg}\cdot^\circ\text{C}$, we can calculate the amount of energy added by using Equation 20.4:

$$Q = m_i c_i \Delta T = (1.00 \times 10^{-3}\text{ kg})(2.090\text{ J/kg}\cdot^\circ\text{C})(30.0^\circ\text{C}) = 62.7\text{ J}$$

Part B. When the temperature of the ice reaches 0.0°C , the ice–water mixture remains at this temperature—even though energy is being added—until all the ice melts. The energy required to melt 1.00 g of ice at 0.0°C is, from Equation 20.6,

$$Q = mL_f = (1.00 \times 10^{-3}\text{ kg})(3.33 \times 10^5\text{ J/kg}) = 333\text{ J}$$

Thus, we have moved to the 396 J ($= 62.7\text{ J} + 333\text{ J}$) mark on the energy axis.

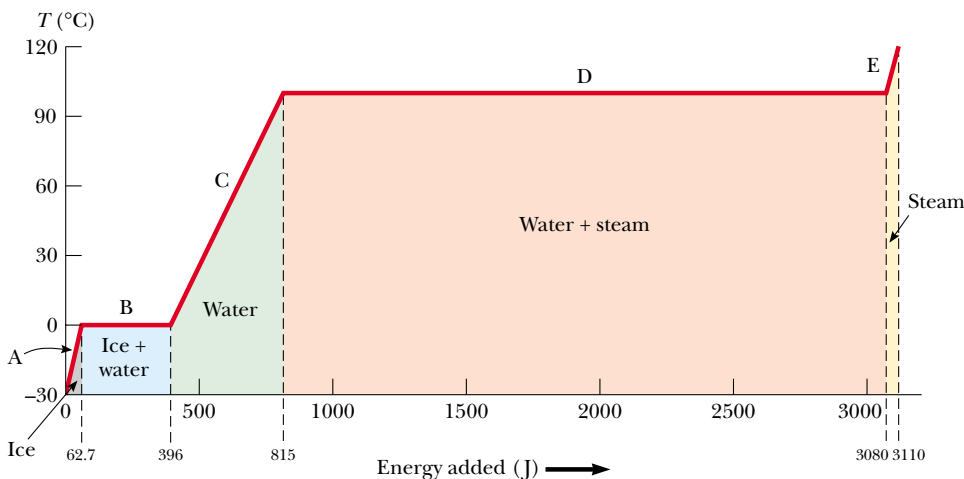


Figure 20.2 A plot of temperature versus energy added when 1.00 g of ice initially at -30.0°C is converted to steam at 120.0°C .

⁴ When a gas cools, it eventually *condenses*—that is, it returns to the liquid phase. The energy given up per unit mass is called the *latent heat of condensation* and is numerically equal to the latent heat of vaporization. Likewise, when a liquid cools, it eventually solidifies, and the *latent heat of solidification* is numerically equal to the latent heat of fusion.

Part C. Between 0.0°C and 100.0°C , nothing surprising happens. No phase change occurs, and so all energy added to the water is used to increase its temperature. The amount of energy necessary to increase the temperature from 0.0°C to 100.0°C is

$$Q = m_w c_w \Delta T = (1.00 \times 10^{-3} \text{ kg})(4.19 \times 10^3 \text{ J/kg}\cdot^{\circ}\text{C})(100.0^{\circ}\text{C}) = 419 \text{ J}$$

Part D. At 100.0°C , another phase change occurs as the water changes from water at 100.0°C to steam at 100.0°C . Similar to the ice–water mixture in part B, the water–steam mixture remains at 100.0°C —even though energy is being added—until all of the liquid has been converted to steam. The energy required to convert 1.00 g of water to steam at 100.0°C is

$$Q = mL_v = (1.00 \times 10^{-3} \text{ kg})(2.26 \times 10^6 \text{ J/kg}) = 2.26 \times 10^3 \text{ J}$$

Part E. On this portion of the curve, as in parts A and C, no phase change occurs; thus, all energy added is used to increase the temperature of the steam. The energy that must be added to raise the temperature of the steam from 100.0°C to 120.0°C is

$$Q = m_s c_s \Delta T = (1.00 \times 10^{-3} \text{ kg})(2.01 \times 10^3 \text{ J/kg}\cdot^{\circ}\text{C})(20.0^{\circ}\text{C}) = 40.2 \text{ J}$$

The total amount of energy that must be added to change 1 g of ice at -30.0°C to steam at 120.0°C is the sum of the results from all five parts of the curve, which is $3.11 \times 10^3 \text{ J}$. Conversely, to cool 1 g of steam at 120.0°C to ice at -30.0°C , we must remove $3.11 \times 10^3 \text{ J}$ of energy.

We can describe phase changes in terms of a rearrangement of molecules when energy is added to or removed from a substance. (For elemental substances in which the atoms do not combine to form molecules, the following discussion should be interpreted in terms of atoms. We use the general term *molecules* to refer to both molecular substances and elemental substances.) Consider first the liquid-to-gas phase change. The molecules in a liquid are close together, and the forces between them are stronger than those between the more widely separated molecules of a gas. Therefore, work must be done on the liquid against these attractive molecular forces if the molecules are to separate. The latent heat of vaporization is the amount of energy per unit mass that must be added to the liquid to accomplish this separation.

Similarly, for a solid, we imagine that the addition of energy causes the amplitude of vibration of the molecules about their equilibrium positions to become greater as the temperature increases. At the melting point of the solid, the amplitude is great enough to break the bonds between molecules and to allow molecules to move to new positions. The molecules in the liquid also are bound to each other, but less strongly than those in the solid phase. The latent heat of fusion is equal to the energy required per unit mass to transform the bonds among all molecules from the solid-type bond to the liquid-type bond.

As you can see from Table 20.2, the latent heat of vaporization for a given substance is usually somewhat higher than the latent heat of fusion. This is not surprising if we consider that the average distance between molecules in the gas phase is much greater than that in either the liquid or the solid phase. In the solid-to-liquid phase change, we transform solid-type bonds between molecules into liquid-type bonds between molecules, which are only slightly less strong. In the liquid-to-gas phase change, however, we break liquid-type bonds and create a situation in which the molecules of the gas essentially are not bonded to each

other. Therefore, it is not surprising that more energy is required to vaporize a given mass of substance than is required to melt it.

Quick Quiz 20.3

Calculate the slopes for the A, C, and E portions of Figure 20.2. Rank the slopes from least to greatest and explain what this ordering means.

Problem-Solving Hints

Calorimetry Problems

If you are having difficulty in solving calorimetry problems, be sure to consider the following points:

- Units of measure must be consistent. For instance, if you are using specific heats measured in $\text{cal/g} \cdot ^\circ\text{C}$, be sure that masses are in grams and temperatures are in Celsius degrees.
- Transfers of energy are given by the equation $Q = mc\Delta T$ only for those processes in which no phase changes occur. Use the equations $Q = mL_f$ and $Q = mL_v$ only when phase changes *are* taking place.
- Often, errors in sign are made when the equation $Q_{\text{cold}} = -Q_{\text{hot}}$ is used. Make sure that you use the negative sign in the equation, and remember that ΔT is always the final temperature minus the initial temperature.

EXAMPLE 20.4 Cooling the Steam

What mass of steam initially at 130°C is needed to warm 200 g of water in a 100-g glass container from 20.0°C to 50.0°C ?

Solution The steam loses energy in three stages. In the first stage, the steam is cooled to 100°C . The energy transfer in the process is

$$\begin{aligned} Q_1 &= m_s c_s \Delta T = m_s (2.01 \times 10^3 \text{ J/kg} \cdot ^\circ\text{C}) (-30.0^\circ\text{C}) \\ &= -m_s (6.03 \times 10^4 \text{ J/kg}) \end{aligned}$$

where m_s is the unknown mass of the steam.

In the second stage, the steam is converted to water. To find the energy transfer during this phase change, we use $Q = -mL_v$, where the negative sign indicates that energy is leaving the steam:

$$Q_2 = -m_s (2.26 \times 10^6 \text{ J/kg})$$

In the third stage, the temperature of the water created from the steam is reduced to 50.0°C . This change requires an energy transfer of

$$\begin{aligned} Q_3 &= m_s c_w \Delta T = m_s (4.19 \times 10^3 \text{ J/kg} \cdot ^\circ\text{C}) (-50.0^\circ\text{C}) \\ &= -m_s (2.09 \times 10^5 \text{ J/kg}) \end{aligned}$$

Adding the energy transfers in these three stages, we obtain

$$\begin{aligned} Q_{\text{hot}} &= Q_1 + Q_2 + Q_3 \\ &= -m_s (6.03 \times 10^4 \text{ J/kg} + 2.26 \times 10^6 \text{ J/kg} \\ &\quad + 2.09 \times 10^5 \text{ J/kg}) \\ &= -m_s (2.53 \times 10^6 \text{ J/kg}) \end{aligned}$$

Now, we turn our attention to the temperature increase of the water and the glass. Using Equation 20.4, we find that

$$\begin{aligned} Q_{\text{cold}} &= (0.200 \text{ kg}) (4.19 \times 10^3 \text{ J/kg} \cdot ^\circ\text{C}) (30.0^\circ\text{C}) \\ &\quad + (0.100 \text{ kg}) (837 \text{ J/kg} \cdot ^\circ\text{C}) (30.0^\circ\text{C}) \\ &= 2.77 \times 10^4 \text{ J} \end{aligned}$$

Using Equation 20.5, we can solve for the unknown mass:

$$\begin{aligned} Q_{\text{cold}} &= -Q_{\text{hot}} \\ 2.77 \times 10^4 \text{ J} &= -[-m_s (2.53 \times 10^6 \text{ J/kg})] \\ m_s &= 1.09 \times 10^{-2} \text{ kg} = 10.9 \text{ g} \end{aligned}$$

EXAMPLE 20.5 Boiling Liquid Helium

Liquid helium has a very low boiling point, 4.2 K, and a very low latent heat of vaporization, $2.09 \times 10^4 \text{ J/kg}$. If energy is transferred to a container of boiling liquid helium from an immersed electric heater at a rate of 10.0 W, how long does it take to boil away 1.00 kg of the liquid?

Solution Because $L_v = 2.09 \times 10^4 \text{ J/kg}$, we must supply $2.09 \times 10^4 \text{ J}$ of energy to boil away 1.00 kg. Because $10.0 \text{ W} = 10.0 \text{ J/s}$, 10.0 J of energy is transferred to the helium each second. Therefore, the time it takes to transfer $2.09 \times 10^4 \text{ J}$

of energy is

$$t = \frac{2.09 \times 10^4 \text{ J}}{10.0 \text{ J/s}} = 2.09 \times 10^3 \text{ s} \approx 35 \text{ min}$$

Exercise If 10.0 W of power is supplied to 1.00 kg of water at 100°C , how long does it take for the water to completely boil away?

Answer 62.8 h.

20.4 WORK AND HEAT IN THERMODYNAMIC PROCESSES

In the macroscopic approach to thermodynamics, we describe the *state* of a system using such variables as pressure, volume, temperature, and internal energy. The number of macroscopic variables needed to characterize a system depends on the nature of the system. For a homogeneous system, such as a gas containing only one type of molecule, usually only two variables are needed. However, it is important to note that a *macroscopic state* of an isolated system can be specified only if the system is in thermal equilibrium internally. In the case of a gas in a container, internal thermal equilibrium requires that every part of the gas be at the same pressure and temperature.

Consider a gas contained in a cylinder fitted with a movable piston (Fig. 20.3). At equilibrium, the gas occupies a volume V and exerts a uniform pressure P on the cylinder's walls and on the piston. If the piston has a cross-sectional area A , the

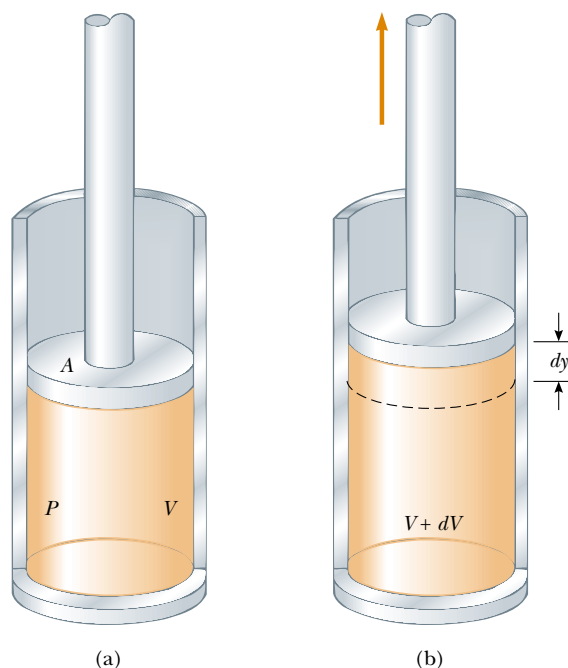


Figure 20.3 Gas contained in a cylinder at a pressure P does work on a moving piston as the system expands from a volume V to a volume $V + dV$.

force exerted by the gas on the piston is $F = PA$. Now let us assume that the gas expands **quasi-statically**, that is, slowly enough to allow the system to remain essentially in thermal equilibrium at all times. As the piston moves up a distance dy , the work done by the gas on the piston is

$$dW = F dy = PA dy$$

Because $A dy$ is the increase in volume of the gas dV , we can express the work done by the gas as

$$dW = P dV \quad (20.7)$$

Because the gas expands, dV is positive, and so the work done by the gas is positive. If the gas were compressed, dV would be negative, indicating that the work done by the gas (which can be interpreted as work done *on* the gas) was negative.

In the thermodynamics problems that we shall solve, we shall identify the system of interest as a substance that is exchanging energy with the environment. In many problems, this will be a gas contained in a vessel; however, we will also consider problems involving liquids and solids. It is an unfortunate fact that, because of the separate historical development of thermodynamics and mechanics, positive work for a thermodynamic system is commonly defined as the work done *by* the system, rather than that done *on* the system. This is the reverse of the case for our study of work in mechanics. Thus, **in thermodynamics, positive work represents a transfer of energy out of the system.** We will use this convention to be consistent with common treatments of thermodynamics.

The total work done by the gas as its volume changes from V_i to V_f is given by the integral of Equation 20.7:

$$W = \int_{V_i}^{V_f} P dV \quad (20.8)$$

To evaluate this integral, it is not enough that we know only the initial and final values of the pressure. We must also know the pressure at every instant during the expansion; we would know this if we had a functional dependence of P with respect to V . This important point is true for any process—the expansion we are discussing here, or any other. To fully specify a process, we must know the values of the thermodynamic variables at every state through which the system passes between the initial and final states. In the expansion we are considering here, we can plot the pressure and volume at each instant to create a PV diagram like the one shown in Figure 20.4. The value of the integral in Equation 20.8 is the area bounded by such a curve. Thus, we can say that

the work done by a gas in the expansion from an initial state to a final state is the area under the curve connecting the states in a PV diagram.

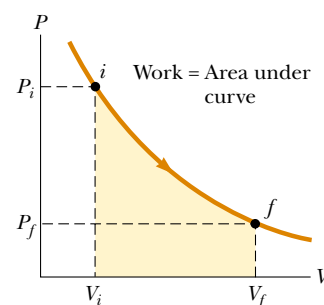


Figure 20.4 A gas expands quasi-statically (slowly) from state i to state f . The work done by the gas equals the area under the PV curve.

Work equals area under the curve in a PV diagram.

As Figure 20.4 shows, the work done in the expansion from the initial state i to the final state f depends on the path taken between these two states, where the *path* on a PV diagram is a description of the thermodynamic process through which the system is taken. To illustrate this important point, consider several paths connecting i and f (Fig. 20.5). In the process depicted in Figure 20.5a, the pressure of the gas is first reduced from P_i to P_f by cooling at constant volume V_i . The gas then expands from V_i to V_f at constant pressure P_f . The value of the work done along this path is equal to the area of the shaded rectangle, which is equal to

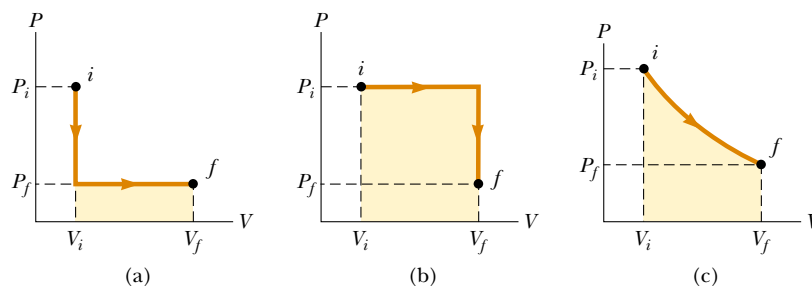


Figure 20.5 The work done by a gas as it is taken from an initial state to a final state depends on the path between these states.

Work done depends on the path between the initial and final states.

$P_f(V_f - V_i)$. In Figure 20.5b, the gas first expands from V_i to V_f at constant pressure P_i . Then, its pressure is reduced to P_f at constant volume V_f . The value of the work done along this path is $P_i(V_f - V_i)$, which is greater than that for the process described in Figure 20.5a. Finally, for the process described in Figure 20.5c, where both P and V change continuously, the work done has some value intermediate between the values obtained in the first two processes. Therefore, we see that **the work done by a system depends on the initial and final states and on the path followed by the system between these states.**

The energy transfer by heat Q into or out of a system also depends on the process. Consider the situations depicted in Figure 20.6. In each case, the gas has the same initial volume, temperature, and pressure and is assumed to be ideal. In Figure 20.6a, the gas is thermally insulated from its surroundings except at the bottom of the gas-filled region, where it is in thermal contact with an energy reservoir. An *energy reservoir* is a source of energy that is considered to be so great that a finite transfer of energy from the reservoir does not change its temperature. The piston is held at its initial position by an external agent—a hand, for instance. When the force with which the piston is held is reduced slightly, the piston rises very slowly to its final position. Because the piston is moving upward, the gas is doing work on

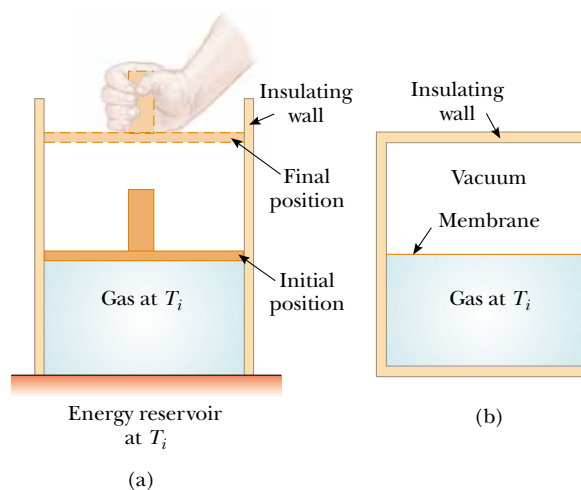


Figure 20.6 (a) A gas at temperature T_i expands slowly while absorbing energy from a reservoir in order to maintain a constant temperature. (b) A gas expands rapidly into an evacuated region after a membrane is broken.

the piston. During this expansion to the final volume V_f , just enough energy is transferred by heat from the reservoir to the gas to maintain a constant temperature T_i .

Now consider the completely thermally insulated system shown in Figure 20.6b. When the membrane is broken, the gas expands rapidly into the vacuum until it occupies a volume V_f and is at a pressure P_f . In this case, the gas does no work because there is no movable piston on which the gas applies a force. Furthermore, no energy is transferred by heat through the insulating wall.

The initial and final states of the ideal gas in Figure 20.6a are identical to the initial and final states in Figure 20.6b, but the paths are different. In the first case, the gas does work on the piston, and energy is transferred slowly to the gas. In the second case, no energy is transferred, and the value of the work done is zero. Therefore, we conclude that **energy transfer by heat, like work done, depends on the initial, final, and intermediate states of the system**. In other words, because heat and work depend on the path, neither quantity is determined solely by the end points of a thermodynamic process.

20.5 THE FIRST LAW OF THERMODYNAMICS

10.6 When we introduced the law of conservation of mechanical energy in Chapter 8, we stated that the mechanical energy of a system is constant in the absence of non-conservative forces such as friction. That is, we did not include changes in the internal energy of the system in this mechanical model. The first law of thermodynamics is a generalization of the law of conservation of energy that encompasses changes in internal energy. It is a universally valid law that can be applied to many processes and provides a connection between the microscopic and macroscopic worlds.

We have discussed two ways in which energy can be transferred between a system and its surroundings. One is work done by the system, which requires that there be a macroscopic displacement of the point of application of a force (or pressure). The other is heat, which occurs through random collisions between the molecules of the system. Both mechanisms result in a change in the internal energy of the system and therefore usually result in measurable changes in the macroscopic variables of the system, such as the pressure, temperature, and volume of a gas.

To better understand these ideas on a quantitative basis, suppose that a system undergoes a change from an initial state to a final state. During this change, energy transfer by heat Q to the system occurs, and work W is done by the system. As an example, suppose that the system is a gas in which the pressure and volume change from P_i and V_i to P_f and V_f . If the quantity $Q - W$ is measured for various paths connecting the initial and final equilibrium states, we find that it is the same for all paths connecting the two states. We conclude that the quantity $Q - W$ is determined completely by the initial and final states of the system, and we call this quantity the **change in the internal energy** of the system. Although Q and W both depend on the path, **the quantity $Q - W$ is independent of the path**. If we use the symbol E_{int} to represent the internal energy, then the *change* in internal energy ΔE_{int} can be expressed as⁵

$$\Delta E_{\text{int}} = Q - W \quad (20.9)$$

⁵ It is an unfortunate accident of history that the traditional symbol for internal energy is U , which is also the traditional symbol for potential energy, as introduced in Chapter 8. To avoid confusion between potential energy and internal energy, we use the symbol E_{int} for internal energy in this book. If you take an advanced course in thermodynamics, however, be prepared to see U used as the symbol for internal energy.



This device, called *Hero's engine*, was invented around 150 B.C. by Hero in Alexandria. When water is boiled in the flask, which is suspended by a cord, steam exits through two tubes at the sides (in opposite directions), creating a torque that rotates the flask.

$Q - W$ is the change in internal energy

First-law equation

where all quantities must have the same units of measure for energy.⁶ Equation 20.9 is known as the **first-law equation** and is a key concept in many applications. As a reminder, we use the convention that Q is positive when energy enters the system and negative when energy leaves the system, and that W is positive when the system does work on the surroundings and negative when work is done on the system.

When a system undergoes an infinitesimal change in state in which a small amount of energy dQ is transferred by heat and a small amount of work dW is done, the internal energy changes by a small amount dE_{int} . Thus, for infinitesimal processes we can express the first-law equation as⁷

$$dE_{\text{int}} = dQ - dW$$

The first-law equation is an energy conservation equation specifying that the only type of energy that changes in the system is the internal energy E_{int} . Let us look at some special cases in which this condition exists.

First, let us consider an *isolated system*—that is, one that does not interact with its surroundings. In this case, no energy transfer by heat takes place and the value of the work done by the system is zero; hence, the internal energy remains constant. That is, because $Q = W = 0$, it follows that $\Delta E_{\text{int}} = 0$, and thus $E_{\text{int},i} = E_{\text{int},f}$. We conclude that **the internal energy E_{int} of an isolated system remains constant.**

Next, we consider the case of a system (one not isolated from its surroundings) that is taken through a **cyclic process**—that is, a process that starts and ends at the same state. In this case, the change in the internal energy must again be zero, and therefore the energy Q added to the system must equal the work W done by the system during the cycle. That is, in a cyclic process,

$$\Delta E_{\text{int}} = 0 \quad \text{and} \quad Q = W$$

On a PV diagram, a cyclic process appears as a closed curve. (The processes described in Figure 20.5 are represented by open curves because the initial and final states differ.) It can be shown that **in a cyclic process, the net work done by the system per cycle equals the area enclosed by the path representing the process on a PV diagram.**

If the value of the work done by the system during some process is zero, then the change in internal energy ΔE_{int} equals the energy transfer Q into or out of the system:

$$\Delta E_{\text{int}} = Q$$

If energy enters the system, then Q is positive and the internal energy increases. For a gas, we can associate this increase in internal energy with an increase in the kinetic energy of the molecules. Conversely, if no energy transfer occurs during some process but work is done by the system, then the change in internal energy equals the negative value of the work done by the system:

$$\Delta E_{\text{int}} = -W$$

⁶ For the definition of work from our mechanics studies, the first law would be written as $\Delta E_{\text{int}} = Q + W$ because energy transfer into the system by either work or heat would increase the internal energy of the system. Because of the reversal of the definition of positive work discussed in Section 20.4, the first law appears as in Equation 20.9, with a minus sign.

⁷ Note that dQ and dW are not true differential quantities; however, dE_{int} is. Because dQ and dW are *inexact differentials*, they are often represented by the symbols δQ and δW . For further details on this point, see an advanced text on thermodynamics, such as R. P. Bauman, *Modern Thermodynamics and Statistical Mechanics*, New York, Macmillan Publishing Co., 1992.

First-law equation for infinitesimal changes

Isolated system

Cyclic process

For example, if a gas is compressed by a moving piston in an insulated cylinder, no energy is transferred by heat and the work done by the gas is negative; thus, the internal energy increases because kinetic energy is transferred from the moving piston to the gas molecules.

On a microscopic scale, no distinction exists between the result of heat and that of work. Both heat and work can produce a change in the internal energy of a system. Although the macroscopic quantities Q and W are *not* properties of a system, they are related to the change of the internal energy of a system through the first-law equation. Once we define a process, or path, we can either calculate or measure Q and W , and we can find the change in the system's internal energy using the first-law equation.

One of the important consequences of the first law of thermodynamics is that there exists a quantity known as internal energy whose value is determined by the state of the system. The internal energy function is therefore called a *state function*.

20.6 SOME APPLICATIONS OF THE FIRST LAW OF THERMODYNAMICS

Before we apply the first law of thermodynamics to specific systems, it is useful for us to first define some common thermodynamic processes. An **adiabatic process** is one during which no energy enters or leaves the system by heat—that is, $Q = 0$. An adiabatic process can be achieved either by thermally insulating the system from its surroundings (as shown in Fig. 20.6b) or by performing the process rapidly, so that there is little time for energy to transfer by heat. Applying the first law of thermodynamics to an adiabatic process, we see that

$$\Delta E_{\text{int}} = -W \quad (\text{adiabatic process}) \quad (20.10)$$

From this result, we see that if a gas expands adiabatically such that W is positive, then ΔE_{int} is negative and the temperature of the gas decreases. Conversely, the temperature of a gas increases when the gas is compressed adiabatically.

Adiabatic processes are very important in engineering practice. Some common examples are the expansion of hot gases in an internal combustion engine, the liquefaction of gases in a cooling system, and the compression stroke in a diesel engine.

The process described in Figure 20.6b, called an **adiabatic free expansion**, is unique. The process is adiabatic because it takes place in an insulated container. Because the gas expands into a vacuum, it does not apply a force on a piston as was depicted in Figure 20.6a, so no work is done on or by the gas. Thus, in this adiabatic process, both $Q = 0$ and $W = 0$. As a result, $\Delta E_{\text{int}} = 0$ for this process, as we can see from the first law. That is, **the initial and final internal energies of a gas are equal in an adiabatic free expansion**. As we shall see in the next chapter, the internal energy of an ideal gas depends only on its temperature. Thus, we expect no change in temperature during an adiabatic free expansion. This prediction is in accord with the results of experiments performed at low pressures. (Experiments performed at high pressures for real gases show a slight decrease or increase in temperature after the expansion. This change is due to intermolecular interactions, which represent a deviation from the model of an ideal gas.)

A process that occurs at constant pressure is called an **isobaric process**. In such a process, the values of the heat and the work are both usually nonzero. The

In an adiabatic process, $Q = 0$.

First-law equation for an adiabatic process

In an adiabatic free expansion, $\Delta E_{\text{int}} = 0$.

In an isobaric process, P remains constant.

work done by the gas is simply

$$W = P(V_f - V_i) \qquad \text{(isobaric process)} \qquad (20.11)$$

where P is the constant pressure.

A process that takes place at constant volume is called an **isovolumetric process**. In such a process, the value of the work done is clearly zero because the volume does not change. Hence, from the first law we see that in an isovolumetric process, because $W = 0$,

$$\Delta E_{\text{int}} = Q \qquad \text{(isovolumetric process)} \qquad (20.12)$$

This expression specifies that **if energy is added by heat to a system kept at constant volume, then all of the transferred energy remains in the system as an increase of the internal energy of the system**. For example, when a can of spray paint is thrown into a fire, energy enters the system (the gas in the can) by heat through the metal walls of the can. Consequently, the temperature, and thus the pressure, in the can increases until the can possibly explodes.

A process that occurs at constant temperature is called an **isothermal process**. A plot of P versus V at constant temperature for an ideal gas yields a hyperbolic curve called an *isotherm*. The internal energy of an ideal gas is a function of temperature only. Hence, in an isothermal process involving an ideal gas, $\Delta E_{\text{int}} = 0$. For an isothermal process, then, we conclude from the first law that the energy transfer Q must be equal to the work done by the gas—that is, $Q = W$. Any energy that enters the system by heat is transferred out of the system by work; as a result, no change of the internal energy of the system occurs.

First-law equation for a constant-volume process

In an isothermal process, T remains constant.

Quick Quiz 20.4

In the last three columns of the following table, fill in the boxes with $-$, $+$, or 0 . For each situation, the system to be considered is identified.

Situation	System	Q	W	ΔE_{int}
(a) Rapidly pumping up a bicycle tire	Air in the pump			
(b) Pan of room-temperature water sitting on a hot stove	Water in the pan			
(c) Air quickly leaking out of a balloon	Air originally in balloon			

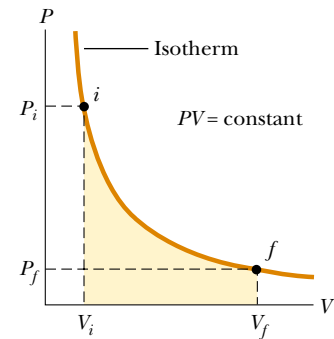


Figure 20.7 The PV diagram for an isothermal expansion of an ideal gas from an initial state to a final state. The curve is a hyperbola.

Isothermal Expansion of an Ideal Gas

Suppose that an ideal gas is allowed to expand quasi-statically at constant temperature, as described by the PV diagram shown in Figure 20.7. The curve is a hyperbola (see Appendix B, Eq. B.23), and the equation of state of an ideal gas with T constant indicates that the equation of this curve is $PV = \text{constant}$. The isothermal expansion of the gas can be achieved by placing the gas in thermal contact with an energy reservoir at the same temperature, as shown in Figure 20.6a.

Let us calculate the work done by the gas in the expansion from state i to state f . The work done by the gas is given by Equation 20.8. Because the gas is ideal and the process is quasi-static, we can use the expression $PV = nRT$ for each point on

the path. Therefore, we have

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

Because T is constant in this case, it can be removed from the integral along with n and R :

$$W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln V \Big|_{V_i}^{V_f}$$

To evaluate the integral, we used $\int (dx/x) = \ln x$. Evaluating this at the initial and final volumes, we have

$$W = nRT \ln \left(\frac{V_f}{V_i} \right) \quad (20.13)$$

Work done by an ideal gas in an isothermal process

Numerically, this work W equals the shaded area under the PV curve shown in Figure 20.7. Because the gas expands, $V_f > V_i$, and the value for the work done by the gas is positive, as we expect. If the gas is compressed, then $V_f < V_i$, and the work done by the gas is negative.

Quick Quiz 20.5

Characterize the paths in Figure 20.8 as isobaric, isovolumetric, isothermal, or adiabatic. Note that $Q = 0$ for path B.

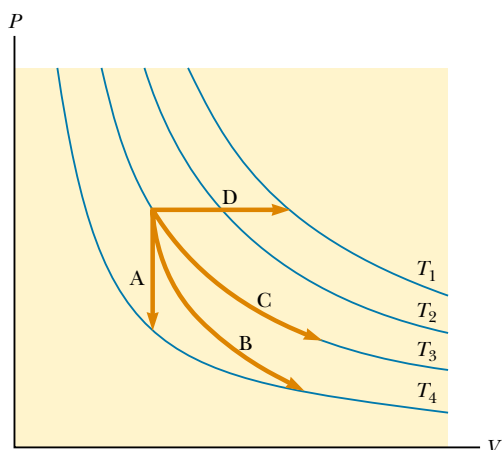


Figure 20.8 Identify the nature of paths A, B, C, and D.

EXAMPLE 20.6 An Isothermal Expansion

A 1.0-mol sample of an ideal gas is kept at 0.0°C during an expansion from 3.0 L to 10.0 L. (a) How much work is done by the gas during the expansion?

Solution Substituting the values into Equation 20.13, we have

$$W = nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$\begin{aligned} W &= (1.0 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(273 \text{ K}) \ln \left(\frac{10.0}{3.0} \right) \\ &= 2.7 \times 10^3 \text{ J} \end{aligned}$$

(b) How much energy transfer by heat occurs with the surroundings in this process?

Solution From the first law, we find that

$$\Delta E_{\text{int}} = Q - W$$

$$0 = Q - W$$

$$Q = W = 2.7 \times 10^3 \text{ J}$$

(c) If the gas is returned to the original volume by means of an isobaric process, how much work is done by the gas?

Solution The work done in an isobaric process is given by Equation 20.11. We are not given the pressure, so we need to incorporate the ideal gas law:

$$\begin{aligned} W &= P(V_f - V_i) = \frac{nRT_i}{V_i} (V_f - V_i) \\ &= \frac{(1.0 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(273 \text{ K})}{10.0 \times 10^{-3} \text{ m}^3} \\ &\quad \times (3.0 \times 10^{-3} \text{ m}^3 - 10.0 \times 10^{-3} \text{ m}^3) \\ &= -1.6 \times 10^3 \text{ J} \end{aligned}$$

Notice that we use the initial temperature and volume to determine the value of the constant pressure because we do not know the final temperature. The work done by the gas is negative because the gas is being compressed.

EXAMPLE 20.7 Boiling Water

Suppose 1.00 g of water vaporizes isobarically at atmospheric pressure ($1.013 \times 10^5 \text{ Pa}$). Its volume in the liquid state is $V_i = V_{\text{liquid}} = 1.00 \text{ cm}^3$, and its volume in the vapor state is $V_f = V_{\text{vapor}} = 1.671 \text{ cm}^3$. Find the work done in the expansion and the change in internal energy of the system. Ignore any mixing of the steam and the surrounding air—imagine that the steam simply pushes the surrounding air out of the way.

Solution Because the expansion takes place at constant pressure, the work done by the system in pushing away the surrounding air is, from Equation 20.11,

$$\begin{aligned} W &= P(V_f - V_i) \\ &= (1.013 \times 10^5 \text{ Pa})(1.671 \times 10^{-6} \text{ m}^3 - 1.00 \times 10^{-6} \text{ m}^3) \\ &= 169 \text{ J} \end{aligned}$$

To determine the change in internal energy, we must know the energy transfer Q needed to vaporize the water. Using Equation 20.6 and the latent heat of vaporization for water, we have

$$Q = mL_v = (1.00 \times 10^{-3} \text{ kg})(2.26 \times 10^6 \text{ J/kg}) = 2.260 \text{ J}$$

Hence, from the first law, the change in internal energy is

$$\Delta E_{\text{int}} = Q - W = 2.260 \text{ J} - 169 \text{ J} = 2.09 \text{ kJ}$$

The positive value for ΔE_{int} indicates that the internal energy of the system increases. We see that most ($2.090 \text{ J}/2.260 \text{ J} = 93\%$) of the energy transferred to the liquid goes into increasing the internal energy of the system. Only $169 \text{ J}/2.260 \text{ J} = 7\%$ leaves the system by work done by the steam on the surrounding atmosphere.

EXAMPLE 20.8 Heating a Solid

A 1.0-kg bar of copper is heated at atmospheric pressure. If its temperature increases from 20°C to 50°C , (a) what is the work done by the copper on the surrounding atmosphere?

Solution Because the process is isobaric, we can find the work done by the copper using Equation 20.11, $W = P(V_f - V_i)$. We can calculate the change in volume of the copper using Equation 19.6. Using the average linear expansion coefficient for copper given in Table 19.2, and remembering that $\beta = 3\alpha$, we obtain

$$\begin{aligned} \Delta V &= \beta V_i \Delta T \\ &= [5.1 \times 10^{-5} (\text{C}^\circ)^{-1}](50^\circ\text{C} - 20^\circ\text{C}) V_i = 1.5 \times 10^{-3} V_i \end{aligned}$$

The volume V_i is equal to m/ρ , and Table 15.1 indicates that the density of copper is $8.92 \times 10^3 \text{ kg/m}^3$. Hence,

$$\Delta V = (1.5 \times 10^{-3}) \left(\frac{1.0 \text{ kg}}{8.92 \times 10^3 \text{ kg/m}^3} \right) = 1.7 \times 10^{-7} \text{ m}^3$$

The work done is

$$\begin{aligned} W &= P\Delta V = (1.013 \times 10^5 \text{ N/m}^2)(1.7 \times 10^{-7} \text{ m}^3) \\ &= 1.7 \times 10^{-2} \text{ J} \end{aligned}$$

(b) What quantity of energy is transferred to the copper by heat?

Solution Taking the specific heat of copper from Table 20.1 and using Equation 20.4, we find that the energy transferred by heat is

$$Q = mc\Delta T = (1.0 \text{ kg})(387 \text{ J/kg}\cdot^\circ\text{C})(30^\circ\text{C}) = 1.2 \times 10^4 \text{ J}$$

(c) What is the increase in internal energy of the copper?

Solution From the first law of thermodynamics, we have

$$\Delta E_{\text{int}} = Q - W = 1.2 \times 10^4 \text{ J} - 1.7 \times 10^{-2} \text{ J} = 1.2 \times 10^4 \text{ J}$$

Note that almost all of the energy transferred into the system by heat goes into increasing the internal energy. The fraction of energy used to do work on the surrounding atmosphere is only about 10^{-6} ! Hence, when analyzing the thermal expansion of a solid or a liquid, the small amount of work done by the system is usually ignored.

20.7 ENERGY TRANSFER MECHANISMS

It is important to understand the rate at which energy is transferred between a system and its surroundings and the mechanisms responsible for the transfer. Therefore, let us now look at three common energy transfer mechanisms that can result in a change in internal energy of a system.

Thermal Conduction

The energy transfer process that is most clearly associated with a temperature difference is **thermal conduction**. In this process, the transfer can be represented on an atomic scale as an exchange of kinetic energy between microscopic particles—molecules, atoms, and electrons—in which less energetic particles gain energy in collisions with more energetic particles. For example, if you hold one end of a long metal bar and insert the other end into a flame, you will find that the temperature of the metal in your hand soon increases. The energy reaches your hand by means of conduction. We can understand the process of conduction by examining what is happening to the microscopic particles in the metal. Initially, before the rod is inserted into the flame, the microscopic particles are vibrating about their equilibrium positions. As the flame heats the rod, those particles near the flame begin to vibrate with greater and greater amplitudes. These particles, in turn, collide with their neighbors and transfer some of their energy in the collisions. Slowly, the amplitudes of vibration of metal atoms and electrons farther and farther from the flame increase until, eventually, those in the metal near your hand are affected. This increased vibration represents an increase in the temperature of the metal and of your potentially burned hand.

The rate of thermal conduction depends on the properties of the substance being heated. For example, it is possible to hold a piece of asbestos in a flame indefinitely. This implies that very little energy is conducted through the asbestos. In general, metals are good thermal conductors, and materials such as asbestos, cork, paper, and fiberglass are poor conductors. Gases also are poor conductors because the separation distance between the particles is so great. Metals are good thermal conductors because they contain large numbers of electrons that are relatively free to move through the metal and so can transport energy over large distances. Thus, in a good conductor, such as copper, conduction takes place both by means of the vibration of atoms and by means of the motion of free electrons.

Conduction occurs only if there is a difference in temperature between two parts of the conducting medium. Consider a slab of material of thickness Δx and cross-sectional area A . One face of the slab is at a temperature T_1 , and the other face is at a temperature $T_2 > T_1$ (Fig. 20.9). Experimentally, it is found that the



Melted snow pattern on a parking lot surface indicates the presence of underground hot water pipes used to aid snow removal. Energy from the water is conducted from the pipes to the pavement, where it causes the snow to melt.

energy Q transferred in a time Δt flows from the hotter face to the colder one. The rate $Q/\Delta t$ at which this energy flows is found to be proportional to the cross-sectional area and the temperature difference $\Delta T = T_2 - T_1$, and inversely proportional to the thickness:

$$\frac{Q}{\Delta t} \propto A \frac{\Delta T}{\Delta x}$$

It is convenient to use the symbol for power \mathcal{P} to represent the **rate of energy transfer**: $\mathcal{P} = Q/\Delta t$. Note that \mathcal{P} has units of watts when Q is in joules and Δt is in seconds. For a slab of infinitesimal thickness dx and temperature difference dT , we can write the **law of thermal conduction** as

$$\mathcal{P} = kA \left| \frac{dT}{dx} \right| \quad (20.14)$$

Law of thermal conduction

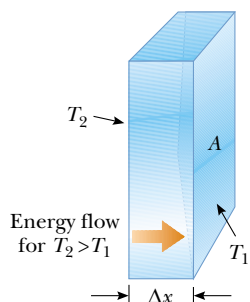


Figure 20.9 Energy transfer through a conducting slab with a cross-sectional area A and a thickness Δx . The opposite faces are at different temperatures T_1 and T_2 .

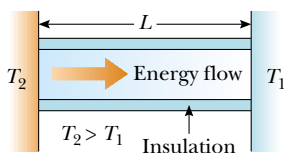


Figure 20.10 Conduction of energy through a uniform, insulated rod of length L . The opposite ends are in thermal contact with energy reservoirs at different temperatures.

where the proportionality constant k is the **thermal conductivity** of the material and $|dT/dx|$ is the **temperature gradient** (the variation of temperature with position).

Suppose that a long, uniform rod of length L is thermally insulated so that energy cannot escape by heat from its surface except at the ends, as shown in Figure 20.10. One end is in thermal contact with an energy reservoir at temperature T_1 , and the other end is in thermal contact with a reservoir at temperature $T_2 > T_1$. When a steady state has been reached, the temperature at each point along the rod is constant in time. In this case if we assume that k is not a function of temperature, the temperature gradient is the same everywhere along the rod and is

$$\left| \frac{dT}{dx} \right| = \frac{T_2 - T_1}{L}$$

Thus the rate of energy transfer by conduction through the rod is

$$\mathcal{P} = kA \frac{(T_2 - T_1)}{L} \quad (20.15)$$

Substances that are good thermal conductors have large thermal conductivity values, whereas good thermal insulators have low thermal conductivity values. Table 20.3 lists thermal conductivities for various substances. Note that metals are generally better thermal conductors than nonmetals are.

Quick Quiz 20.6

Will an ice cube wrapped in a wool blanket remain frozen for (a) a shorter length of time, (b) the same length of time, or (c) a longer length of time than an identical ice cube exposed to air at room temperature?

For a compound slab containing several materials of thicknesses L_1, L_2, \dots and thermal conductivities k_1, k_2, \dots , the rate of energy transfer through the slab at steady state is

$$\mathcal{P} = \frac{A(T_2 - T_1)}{\sum_i (L_i/k_i)} \quad (20.16)$$

TABLE 20.3 Thermal Conductivities

Substance	Thermal Conductivity (W/m · °C)
Metals (at 25°C)	
Aluminum	238
Copper	397
Gold	314
Iron	79.5
Lead	34.7
Silver	427
Nonmetals (approximate values)	
Asbestos	0.08
Concrete	0.8
Diamond	2 300
Glass	0.8
Ice	2
Rubber	0.2
Water	0.6
Wood	0.08
Gases (at 20°C)	
Air	0.023 4
Helium	0.138
Hydrogen	0.172
Nitrogen	0.023 4
Oxygen	0.023 8

where T_1 and T_2 are the temperatures of the outer surfaces (which are held constant) and the summation is over all slabs. The following example shows how this equation results from a consideration of two thicknesses of materials.

EXAMPLE 20.9 Energy Transfer Through Two Slabs

Two slabs of thickness L_1 and L_2 and thermal conductivities k_1 and k_2 are in thermal contact with each other, as shown in Figure 20.11. The temperatures of their outer surfaces are T_1 and T_2 , respectively, and $T_2 > T_1$. Determine the temperature at the interface and the rate of energy transfer by conduction through the slabs in the steady-state condition.

Solution If T is the temperature at the interface, then the rate at which energy is transferred through slab 1 is

$$(1) \quad \mathcal{P}_1 = \frac{k_1 A (T - T_1)}{L_1}$$

The rate at which energy is transferred through slab 2 is

$$(2) \quad \mathcal{P}_2 = \frac{k_2 A (T_2 - T)}{L_2}$$

When a steady state is reached, these two rates must be equal; hence,

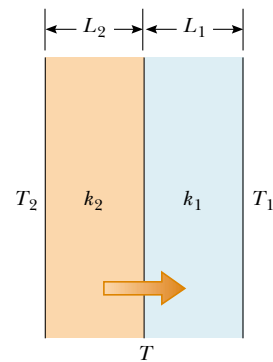


Figure 20.11 Energy transfer by conduction through two slabs in thermal contact with each other. At steady state, the rate of energy transfer through slab 1 equals the rate of energy transfer through slab 2.

$$\frac{k_1 A (T - T_1)}{L_1} = \frac{k_2 A (T_2 - T)}{L_2}$$

Solving for T gives

$$(3) \quad T = \frac{k_1 L_2 T_1 + k_2 L_1 T_2}{k_1 L_2 + k_2 L_1}$$

Substituting (3) into either (1) or (2), we obtain

$$\mathcal{P} = \frac{A (T_2 - T_1)}{(L_1/k_1) + (L_2/k_2)}$$

Extension of this model to several slabs of materials leads to Equation 20.16.

Home Insulation

In engineering practice, the term L/k for a particular substance is referred to as the **R value** of the material. Thus, Equation 20.16 reduces to

$$\mathcal{P} = \frac{A (T_2 - T_1)}{\sum_i R_i} \tag{20.17}$$



Energy is conducted from the inside to the exterior more rapidly on the part of the roof where the snow has melted. The dormer appears to have been added and insulated. The main roof does not appear to be well insulated.

where $R_i = L_i/k_i$. The R values for a few common building materials are given in Table 20.4. In the United States, the insulating properties of materials used in buildings are usually expressed in engineering units, not SI units. Thus, in Table 20.4, measurements of R values are given as a combination of British thermal units, feet, hours, and degrees Fahrenheit.

At any vertical surface open to the air, a very thin stagnant layer of air adheres to the surface. One must consider this layer when determining the R value for a wall. The thickness of this stagnant layer on an outside wall depends on the speed of the wind. Energy loss from a house on a windy day is greater than the loss on a day when the air is calm. A representative R value for this stagnant layer of air is given in Table 20.4.

TABLE 20.4 R Values for Some Common Building Materials

Material	R value (ft ² · °F · h/Btu)
Hardwood siding (1 in. thick)	0.91
Wood shingles (lapped)	0.87
Brick (4 in. thick)	4.00
Concrete block (filled cores)	1.93
Fiberglass batting (3.5 in. thick)	10.90
Fiberglass batting (6 in. thick)	18.80
Fiberglass board (1 in. thick)	4.35
Cellulose fiber (1 in. thick)	3.70
Flat glass (0.125 in. thick)	0.89
Insulating glass (0.25-in. space)	1.54
Air space (3.5 in. thick)	1.01
Stagnant air layer	0.17
Drywall (0.5 in. thick)	0.45
Sheathing (0.5 in. thick)	1.32



This thermogram of a home, made during cold weather, shows colors ranging from white and orange (areas of greatest energy loss) to blue and purple (areas of least energy loss).

EXAMPLE 20.10 The R Value of a Typical Wall

Calculate the total R value for a wall constructed as shown in Figure 20.12a. Starting outside the house (toward the front in the figure) and moving inward, the wall consists of 4-in. brick, 0.5-in. sheathing, an air space 3.5 in. thick, and 0.5-in. drywall. Do not forget the stagnant air layers inside and outside the house.

Solution Referring to Table 20.4, we find that

R_1 (outside stagnant air layer)	$= 0.17 \text{ ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
R_2 (brick)	$= 4.00 \text{ ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
R_3 (sheathing)	$= 1.32 \text{ ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
R_4 (air space)	$= 1.01 \text{ ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
R_5 (drywall)	$= 0.45 \text{ ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
R_6 (inside stagnant air layer)	$= 0.17 \text{ ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$

R_{total}	$= 7.12 \text{ ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
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Exercise If a layer of fiberglass insulation 3.5 in. thick is placed inside the wall to replace the air space, as shown in Figure 20.12b, what is the new total R value? By what factor is the energy loss reduced?

Answer $R = 17 \text{ ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$; 2.4.

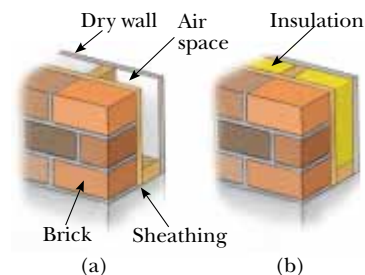


Figure 20.12 An exterior house wall containing (a) an air space and (b) insulation.

Convection

At one time or another, you probably have warmed your hands by holding them over an open flame. In this situation, the air directly above the flame is heated and expands. As a result, the density of this air decreases and the air rises. This warmed mass of air heats your hands as it flows by. **Energy transferred by the movement of a heated substance is said to have been transferred by convection.** When the movement results from differences in density, as with air around a fire, it is referred to as *natural convection*. Air flow at a beach is an example of natural convection, as is the mixing that occurs as surface water in a lake cools and sinks (see

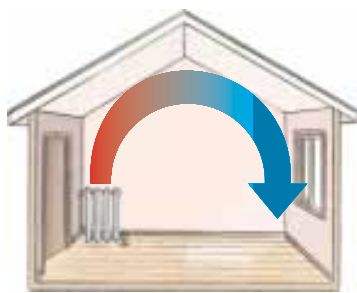


Figure 20.13 Convection currents are set up in a room heated by a radiator.

Stefan's law

Chapter 19). When the heated substance is forced to move by a fan or pump, as in some hot-air and hot-water heating systems, the process is called *forced convection*.

If it were not for convection currents, it would be very difficult to boil water. As water is heated in a teakettle, the lower layers are warmed first. The heated water expands and rises to the top because its density is lowered. At the same time, the denser, cool water at the surface sinks to the bottom of the kettle and is heated.

The same process occurs when a room is heated by a radiator. The hot radiator warms the air in the lower regions of the room. The warm air expands and rises to the ceiling because of its lower density. The denser, cooler air from above sinks, and the continuous air current pattern shown in Figure 20.13 is established.

Radiation

The third means of energy transfer that we shall discuss is **radiation**. All objects radiate energy continuously in the form of electromagnetic waves (see Chapter 34) produced by thermal vibrations of the molecules. You are likely familiar with electromagnetic radiation in the form of the orange glow from an electric stove burner, an electric space heater, or the coils of a toaster.

The rate at which an object radiates energy is proportional to the fourth power of its absolute temperature. This is known as **Stefan's law** and is expressed in equation form as

$$\mathcal{P} = \sigma A e T^4 \quad (20.18)$$

where \mathcal{P} is the power in watts radiated by the object, σ is a constant equal to $5.669\,6 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$, A is the surface area of the object in square meters, e is the **emissivity** constant, and T is the surface temperature in kelvins. The value of e can vary between zero and unity, depending on the properties of the surface of the object. The emissivity is equal to the fraction of the incoming radiation that the surface absorbs.

Approximately $1\,340 \text{ J}$ of electromagnetic radiation from the Sun passes perpendicularly through each 1 m^2 at the top of the Earth's atmosphere every second. This radiation is primarily visible and infrared light accompanied by a significant amount of ultraviolet radiation. We shall study these types of radiation in detail in Chapter 34. Some of this energy is reflected back into space, and some is absorbed by the atmosphere. However, enough energy arrives at the surface of the Earth each day to supply all our energy needs on this planet hundreds of times over—if only it could be captured and used efficiently. The growth in the number of solar energy-powered houses built in this country reflects the increasing efforts being made to use this abundant energy. Radiant energy from the Sun affects our day-to-day existence in a number of ways. For example, it influences the Earth's average temperature, ocean currents, agriculture, and rain patterns.

What happens to the atmospheric temperature at night is another example of the effects of energy transfer by radiation. If there is a cloud cover above the Earth, the water vapor in the clouds absorbs part of the infrared radiation emitted by the Earth and re-emits it back to the surface. Consequently, temperature levels at the surface remain moderate. In the absence of this cloud cover, there is nothing to prevent this radiation from escaping into space; thus the temperature decreases more on a clear night than on a cloudy one.

As an object radiates energy at a rate given by Equation 20.18, it also absorbs electromagnetic radiation. If the latter process did not occur, an object would eventually radiate all its energy, and its temperature would reach absolute zero. The energy an object absorbs comes from its surroundings, which consist of other objects that radiate energy. If an object is at a temperature T and its surroundings

are at a temperature T_0 , then the net energy gained or lost each second by the object as a result of radiation is

$$\mathcal{P}_{\text{net}} = \sigma A e (T^4 - T_0^4) \quad (20.19)$$

When an object is in equilibrium with its surroundings, it radiates and absorbs energy at the same rate, and so its temperature remains constant. When an object is hotter than its surroundings, it radiates more energy than it absorbs, and its temperature decreases. An **ideal absorber** is defined as an object that absorbs all the energy incident on it, and for such a body, $e = 1$. Such an object is often referred to as a **black body**. An ideal absorber is also an ideal radiator of energy. In contrast, an object for which $e = 0$ absorbs none of the energy incident on it. Such an object reflects all the incident energy, and thus is an **ideal reflector**.

The Dewar Flask

The *Dewar flask*⁸ is a container designed to minimize energy losses by conduction, convection, and radiation. Such a container is used to store either cold or hot liquids for long periods of time. (A Thermos bottle is a common household equivalent of a Dewar flask.) The standard construction (Fig. 20.14) consists of a double-walled Pyrex glass vessel with silvered walls. The space between the walls is evacuated to minimize energy transfer by conduction and convection. The silvered surfaces minimize energy transfer by radiation because silver is a very good reflector and has very low emissivity. A further reduction in energy loss is obtained by reducing the size of the neck. Dewar flasks are commonly used to store liquid nitrogen (boiling point: 77 K) and liquid oxygen (boiling point: 90 K).

To confine liquid helium (boiling point: 4.2 K), which has a very low heat of vaporization, it is often necessary to use a double Dewar system in which the Dewar flask containing the liquid is surrounded by a second Dewar flask. The space between the two flasks is filled with liquid nitrogen.

Newer designs of storage containers use “super insulation” that consists of many layers of reflecting material separated by fiberglass. All of this is in a vacuum, and no liquid nitrogen is needed with this design.

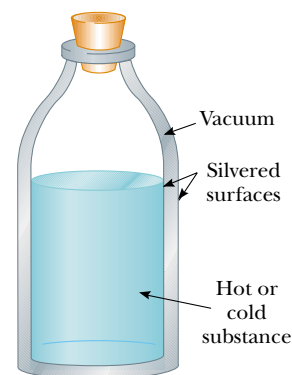


Figure 20.14 A cross-sectional view of a Dewar flask, which is used to store hot or cold substances.

EXAMPLE 20.11 Who Turned Down the Thermostat?

A student is trying to decide what to wear. The surroundings (his bedroom) are at 20.0°C . If the skin temperature of the unclothed student is 35°C , what is the net energy loss from his body in 10.0 min by radiation? Assume that the emissivity of skin is 0.900 and that the surface area of the student is 1.50 m^2 .

Solution Using Equation 20.19, we find that the net rate of energy loss from the skin is

$$\begin{aligned} \mathcal{P}_{\text{net}} &= \sigma A e (T^4 - T_0^4) \\ &= (5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4) (1.50 \text{ m}^2) \\ &\quad \times (0.900) [(308 \text{ K})^4 - (293 \text{ K})^4] = 125 \text{ W} \end{aligned}$$

(Why is the temperature given in kelvins?) At this rate, the total energy lost by the skin in 10 min is

$$Q = \mathcal{P}_{\text{net}} \times \Delta t = (125 \text{ W})(600 \text{ s}) = 7.5 \times 10^4 \text{ J}$$

Note that the energy radiated by the student is roughly equivalent to that produced by two 60-W light bulbs!

⁸ Invented by Sir James Dewar (1842–1923).

SUMMARY

Internal energy is all of a system's energy that is associated with the system's microscopic components. Internal energy includes kinetic energy of translation, rotation, and vibration of molecules, potential energy within molecules, and potential energy between molecules.

Heat is the transfer of energy across the boundary of a system resulting from a temperature difference between the system and its surroundings. We use the symbol Q for the amount of energy transferred by this process.

The **calorie** is the amount of energy necessary to raise the temperature of 1 g of water from 14.5°C to 15.5°C. The **mechanical equivalent of heat** is 1 cal = 4.186 J.

The **heat capacity** C of any sample is the amount of energy needed to raise the temperature of the sample by 1°C. The energy Q required to change the temperature of a mass m of a substance by an amount ΔT is

$$Q = mc\Delta T \quad (20.4)$$

where c is the **specific heat** of the substance.

The energy required to change the phase of a pure substance of mass m is

$$Q = mL \quad (20.6)$$

where L is the **latent heat** of the substance and depends on the nature of the phase change and the properties of the substance.

The **work done** by a gas as its volume changes from some initial value V_i to some final value V_f is

$$W = \int_{V_i}^{V_f} P dV \quad (20.8)$$

where P is the pressure, which may vary during the process. In order to evaluate W , the process must be fully specified—that is, P and V must be known during each step. In other words, the work done depends on the path taken between the initial and final states.

The **first law of thermodynamics** states that when a system undergoes a change from one state to another, the change in its internal energy is

$$\Delta E_{\text{int}} = Q - W \quad (20.9)$$

where Q is the energy transferred into the system by heat and W is the work done by the system. Although Q and W both depend on the path taken from the initial state to the final state, the quantity ΔE_{int} is path-independent. This central equation is a statement of conservation of energy that includes changes in internal energy.

In a **cyclic process** (one that originates and terminates at the same state), $\Delta E_{\text{int}} = 0$ and, therefore, $Q = W$. That is, the energy transferred into the system by heat equals the work done by the system during the process.

In an **adiabatic process**, no energy is transferred by heat between the system and its surroundings ($Q = 0$). In this case, the first law gives $\Delta E_{\text{int}} = -W$. That is, the internal energy changes as a consequence of work being done by the system. In the **adiabatic free expansion** of a gas, $Q = 0$ and $W = 0$; thus, $\Delta E_{\text{int}} = 0$. That is, the internal energy of the gas does not change in such a process.

An **isobaric process** is one that occurs at constant pressure. The work done in such a process is $W = P(V_f - V_i)$.

An **isovolumetric process** is one that occurs at constant volume. No work is done in such a process, so $\Delta E_{\text{int}} = Q$.

An **isothermal process** is one that occurs at constant temperature. The work done by an ideal gas during an isothermal process is

$$W = nRT \ln\left(\frac{V_f}{V_i}\right) \quad (20.13)$$

Energy may be transferred by work, which we addressed in Chapter 7, and by conduction, convection, or radiation. **Conduction** can be viewed as an exchange of kinetic energy between colliding molecules or electrons. The rate at which energy flows by conduction through a slab of area A is

$$\mathcal{P} = kA \left| \frac{dT}{dx} \right| \quad (20.14)$$

where k is the **thermal conductivity** of the material from which the slab is made and $|dT/dx|$ is the **temperature gradient**. This equation can be used in many situations in which the rate of transfer of energy through materials is important.

In **convection**, a heated substance moves from one place to another.

All bodies emit **radiation** in the form of electromagnetic waves at the rate

$$\mathcal{P} = \sigma A \epsilon T^4 \quad (20.18)$$

A body that is hotter than its surroundings radiates more energy than it absorbs, whereas a body that is cooler than its surroundings absorbs more energy than it radiates.

QUESTIONS

1. The specific heat of water is about two times that of ethyl alcohol. Equal masses of alcohol and water are contained in separate beakers and are supplied with the same amount of energy. Compare the temperature increases of the two liquids.
2. Give one reason why coastal regions tend to have a more moderate climate than inland regions do.
3. A small metal crucible is taken from a 200°C oven and immersed in a tub full of water at room temperature (this process is often referred to as *quenching*). What is the approximate final equilibrium temperature?
4. What is the major problem that arises in measuring specific heats if a sample with a temperature greater than 100°C is placed in water?
5. In a daring lecture demonstration, an instructor dips his wetted fingers into molten lead (327°C) and withdraws them quickly, without getting burned. How is this possible? (This is a dangerous experiment that you should *not* attempt.)
6. The pioneers found that placing a large tub of water in a storage cellar would prevent their food from freezing on really cold nights. Explain why.
7. What is wrong with the statement, "Given any two bodies, the one with the higher temperature contains more heat."
8. Why is it possible for you to hold a lighted match, even when it is burned to within a few millimeters of your fingertips?
9. Why is it more comfortable to hold a cup of hot tea by the handle than by wrapping your hands around the cup itself?

10. Figure Q20.10 shows a pattern formed by snow on the roof of a barn. What causes the alternating pattern of snowcover and exposed roof?



Figure Q20.10 Alternating pattern on a snow-covered roof.


11. Why is a person able to remove a piece of dry aluminum foil from a hot oven with bare fingers but burns his or her fingers if there is moisture on the foil?
12. A tile floor in a bathroom may feel uncomfortably cold to your bare feet, but a carpeted floor in an adjoining room at the same temperature feels warm. Why?

13. Why can potatoes be baked more quickly when a metal skewer has been inserted through them?
14. Explain why a Thermos bottle has silvered walls and a vacuum jacket.
15. A piece of paper is wrapped around a rod made half of wood and half of copper. When held over a flame, the paper in contact with the wood burns but the paper in contact with the metal does not. Explain.
16. Why is it necessary to store liquid nitrogen or liquid oxygen in vessels equipped with either polystyrene insulation or a double-evacuated wall?
17. Why do heavy draperies hung over the windows help keep a home warm in the winter and cool in the summer?
18. If you wish to cook a piece of meat thoroughly on an open fire, why should you not use a high flame? (Note: Carbon is a good thermal insulator.)
19. When insulating a wood-frame house, is it better to place the insulation against the cooler, outside wall or against the warmer, inside wall? (In either case, an air barrier must be considered.)
20. In an experimental house, polystyrene beads were pumped into the air space between the panes of glass in double-pane windows at night in the winter, and they were pumped out to holding bins during the day. How would this procedure assist in conserving energy in the house?
21. Pioneers stored fruits and vegetables in underground cellars. Discuss the advantages of choosing this location as a storage site.
22. Concrete has a higher specific heat than soil does. Use this fact to explain (partially) why cities have a higher average night-time temperature than the surrounding countryside does. If a city is hotter than the surrounding countryside, would you expect breezes to blow from city to country or from country to city? Explain.
23. When camping in a canyon on a still night, a hiker notices that a breeze begins to stir as soon as the Sun strikes the surrounding peaks. What causes the breeze?
24. Updrafts of air are familiar to all pilots and are used to keep non-motorized gliders aloft. What causes these currents?
25. If water is a poor thermal conductor, why can it be heated quickly when placed over a flame?
26. The United States penny is now made of copper-coated zinc. Can a calorimetric experiment be devised to test for the metal content in a collection of pennies? If so, describe such a procedure.
27. If you hold water in a paper cup over a flame, you can bring the water to a boil without burning the cup. How is this possible?
28. When a sealed Thermos bottle full of hot coffee is shaken, what are the changes, if any, in (a) the temperature of the coffee and (b) the internal energy of the coffee?
29. Using the first law of thermodynamics, explain why the total energy of an isolated system is always constant.
30. Is it possible to convert internal energy into mechanical energy? Explain using examples.
31. Suppose that you pour hot coffee for your guests and one of them chooses to drink the coffee after it has been in the cup for several minutes. For the coffee to be warmest, should the person add the cream just after the coffee is poured or just before drinking it? Explain.
32. Suppose that you fill two identical cups both at room temperature with the same amount of hot coffee. One cup contains a metal spoon, while the other does not. If you wait for several minutes, which of the two contains the warmer coffee? Which energy transfer process accounts for this result?
33. A warning sign often seen on highways just before a bridge is "Caution—Bridge Surface Freezes Before Road Surface." Which of the three energy transfer processes is most important in causing a bridge surface to freeze before a road surface on very cold days?

PROBLEMS

1, 2, 3 = straightforward, intermediate, challenging □ = full solution available in the *Student Solutions Manual and Study Guide*

WEB = solution posted at <http://www.saunderscollege.com/physics/>  = Computer useful in solving problem  Interactive Physics

 = paired numerical/symbolic problems

Section 20.1 Heat and Internal Energy

1. Water at the top of Niagara Falls has a temperature of 10.0°C . It falls through a distance of 50.0 m. Assuming that all of its potential energy goes into warming of the water, calculate the temperature of the water at the bottom of the Falls.
2. Consider Joule's apparatus described in Figure 20.1. Each of the two masses is 1.50 kg, and the tank is filled with 200 g of water. What is the increase in the temperature of the water after the masses fall through a distance of 3.00 m?

Section 20.2 Heat Capacity and Specific Heat

3. The temperature of a silver bar rises by 10.0°C when it absorbs 1.23 kJ of energy by heat. The mass of the bar is 525 g. Determine the specific heat of silver.
4. A 50.0-g sample of copper is at 25.0°C . If 1 200 J of energy is added to it by heat, what is its final temperature?
- WEB 5. A 1.50-kg iron horseshoe initially at 600°C is dropped into a bucket containing 20.0 kg of water at 25.0°C . What is the final temperature? (Neglect the heat capacity of the container and assume that a negligible amount of water boils away.)

6. An aluminum cup with a mass of 200 g contains 800 g of water in thermal equilibrium at 80.0°C . The combination of cup and water is cooled uniformly so that the temperature decreases at a rate of $1.50^\circ\text{C}/\text{min}$. At what rate is energy being removed by heat? Express your answer in watts.
7. An aluminum calorimeter with a mass of 100 g contains 250 g of water. The calorimeter and water are in thermal equilibrium at 10.0°C . Two metallic blocks are placed into the water. One is a 50.0-g piece of copper at 80.0°C ; the other block has a mass of 70.0 g and is originally at a temperature of 100°C . The entire system stabilizes at a final temperature of 20.0°C . (a) Determine the specific heat of the unknown sample. (b) Guess the material of the unknown, using the data given in Table 20.1.
8. Lake Erie contains roughly $4.00 \times 10^{11} \text{ m}^3$ of water. (a) How much energy is required to raise the temperature of this volume of water from 11.0°C to 12.0°C ? (b) Approximately how many years would it take to supply this amount of energy with the use of a 1 000-MW wasted energy output of an electric power plant?
9. A 3.00-g copper penny at 25.0°C drops from a height of 50.0 m to the ground. (a) If 60.0% of the change in potential energy goes into increasing the internal energy, what is its final temperature? (b) Does the result you obtained in (a) depend on the mass of the penny? Explain.
10. If a mass m_h of water at T_h is poured into an aluminum cup of mass m_{Al} containing mass m_c of water at T_c , where $T_h > T_c$, what is the equilibrium temperature of the system?
11. A water heater is operated by solar power. If the solar collector has an area of 6.00 m^2 and the power delivered by sunlight is $550 \text{ W}/\text{m}^2$, how long does it take to increase the temperature of 1.00 m^3 of water from 20.0°C to 60.0°C ?

Section 20.3 Latent Heat

12. How much energy is required to change a 40.0-g ice cube from ice at -10.0°C to steam at 110°C ?
13. A 3.00-g lead bullet at 30.0°C is fired at a speed of 240 m/s into a large block of ice at 0°C , in which it becomes embedded. What quantity of ice melts?
14. Steam at 100°C is added to ice at 0°C . (a) Find the amount of ice melted and the final temperature when the mass of steam is 10.0 g and the mass of ice is 50.0 g. (b) Repeat this calculation, taking the mass of steam as 1.00 g and the mass of ice as 50.0 g.
15. A 1.00-kg block of copper at 20.0°C is dropped into a large vessel of liquid nitrogen at 77.3 K. How many kilograms of nitrogen boil away by the time the copper reaches 77.3 K? (The specific heat of copper is $0.0920 \text{ cal}/\text{g} \cdot ^\circ\text{C}$. The latent heat of vaporization of nitrogen is $48.0 \text{ cal}/\text{g}$.)
16. A 50.0-g copper calorimeter contains 250 g of water at 20.0°C . How much steam must be condensed into the water if the final temperature of the system is to reach 50.0°C ?
- WEB 17. In an insulated vessel, 250 g of ice at 0°C is added to 600 g of water at 18.0°C . (a) What is the final temperature of the system? (b) How much ice remains when the system reaches equilibrium?
18. **Review Problem.** Two speeding lead bullets, each having a mass of 5.00 g, a temperature of 20.0°C , and a speed of 500 m/s, collide head-on. Assuming a perfectly inelastic collision and no loss of energy to the atmosphere, describe the final state of the two-bullet system.
19. If 90.0 g of molten lead at 327.3°C is poured into a 300-g casting form made of iron and initially at 20.0°C , what is the final temperature of the system? (Assume that no energy loss to the environment occurs.)

Section 20.4 Work and Heat in Thermodynamic Processes

20. Gas in a container is at a pressure of 1.50 atm and a volume of 4.00 m^3 . What is the work done by the gas (a) if it expands at constant pressure to twice its initial volume? (b) If it is compressed at constant pressure to one quarter of its initial volume?

- WEB 21. A sample of ideal gas is expanded to twice its original volume of 1.00 m^3 in a quasi-static process for which $P = \alpha V^2$, with $\alpha = 5.00 \text{ atm}/\text{m}^6$, as shown in Figure P20.21. How much work is done by the expanding gas?

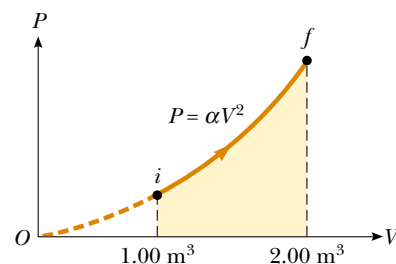


Figure P20.21

22. (a) Determine the work done by a fluid that expands from i to f as indicated in Figure P20.22. (b) How much

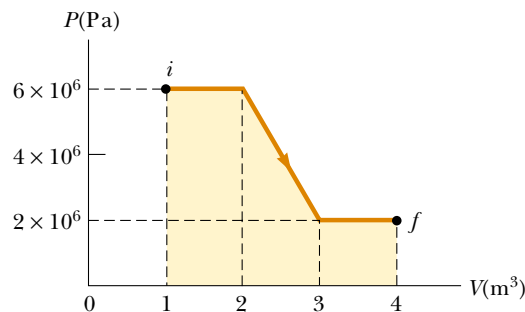


Figure P20.22

work is performed by the fluid if it is compressed from f to i along the same path?

23. One mole of an ideal gas is heated slowly so that it goes from PV state (P_i, V_i) to $(3P_i, 3V_i)$ in such a way that the pressure of the gas is directly proportional to the volume. (a) How much work is done in the process? (b) How is the temperature of the gas related to its volume during this process?
24. A sample of helium behaves as an ideal gas as energy is added by heat at constant pressure from 273 K to 373 K. If the gas does 20.0 J of work, what is the mass of helium present?
- WEB 25. An ideal gas is enclosed in a cylinder with a movable piston on top. The piston has a mass of 8 000 g and an area of 5.00 cm^2 and is free to slide up and down, keeping the pressure of the gas constant. How much work is done as the temperature of 0.200 mol of the gas is raised from 20.0°C to 300°C ?
26. An ideal gas is enclosed in a cylinder that has a movable piston on top. The piston has a mass m and an area A and is free to slide up and down, keeping the pressure of the gas constant. How much work is done as the temperature of n mol of the gas is raised from T_1 to T_2 ?
27. A gas expands from I to F along three possible paths, as indicated in Figure P20.27. Calculate the work in joules done by the gas along the paths IAF , IF , and IBF .

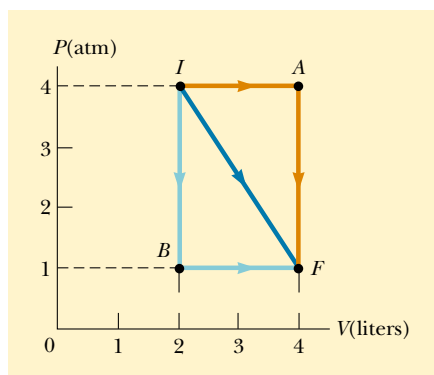


Figure P20.27

Section 20.5 The First Law of Thermodynamics

28. A gas is compressed from 9.00 L to 2.00 L at a constant pressure of 0.800 atm. In the process, 400 J of energy leaves the gas by heat. (a) What is the work done by the gas? (b) What is the change in its internal energy?
29. A thermodynamic system undergoes a process in which its internal energy decreases by 500 J. If, at the same time, 220 J of work is done on the system, what is the energy transferred to or from it by heat?
30. A gas is taken through the cyclic process described in Figure P20.30. (a) Find the net energy transferred to the system by heat during one complete cycle. (b) If the

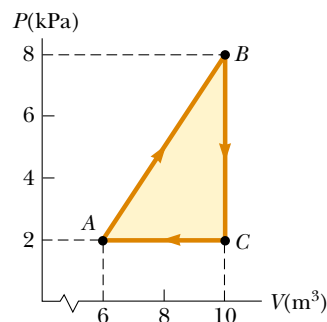


Figure P20.30 Problems 30 and 31.

- cycle is reversed—that is, if the process follows the path $ACBA$ —what is the net energy input per cycle by heat?
31. Consider the cyclic process depicted in Figure P20.30. If Q is negative for the process BC , and if ΔE_{int} is negative for the process CA , what are the signs of Q , W , and ΔE_{int} that are associated with each process?
32. A sample of an ideal gas goes through the process shown in Figure P20.32. From A to B , the process is adiabatic; from B to C , it is isobaric, with 100 kJ of energy flowing into the system by heat. From C to D , the process is isothermal; from D to A , it is isobaric, with 150 kJ of energy flowing out of the system by heat. Determine the difference in internal energy, $E_{\text{int}, B} - E_{\text{int}, A}$.

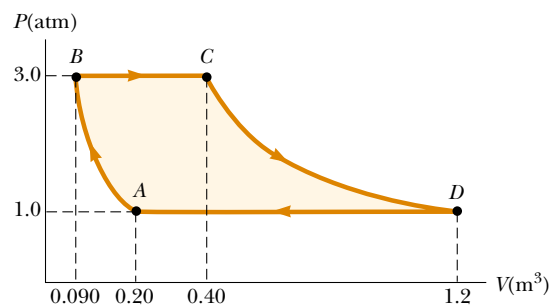


Figure P20.32

Section 20.6 Some Applications of the First Law of Thermodynamics

33. An ideal gas initially at 300 K undergoes an isobaric expansion at 2.50 kPa. If the volume increases from 1.00 m^3 to 3.00 m^3 and if 12.5 kJ of energy is transferred to the gas by heat, what are (a) the change in its internal energy and (b) its final temperature?
34. One mole of an ideal gas does 3 000 J of work on its surroundings as it expands isothermally to a final pressure of 1.00 atm and a volume of 25.0 L. Determine (a) the initial volume and (b) the temperature of the gas.
35. How much work is done by the steam when 1.00 mol of water at 100°C boils and becomes 1.00 mol of steam at

100°C and at 1.00 atm pressure? Assuming the steam to be an ideal gas, determine the change in internal energy of the steam as it vaporizes.

36. A 1.00-kg block of aluminum is heated at atmospheric pressure such that its temperature increases from 22.0°C to 40.0°C. Find (a) the work done by the aluminum, (b) the energy added to it by heat, and (c) the change in its internal energy.
37. A 2.00-mol sample of helium gas initially at 300 K and 0.400 atm is compressed isothermally to 1.20 atm. Assuming the behavior of helium to be that of an ideal gas, find (a) the final volume of the gas, (b) the work done by the gas, and (c) the energy transferred by heat.
38. One mole of water vapor at a temperature of 373 K cools down to 283 K. The energy given off from the cooling vapor by heat is absorbed by 10.0 mol of an ideal gas, causing it to expand at a constant temperature of 273 K. If the final volume of the ideal gas is 20.0 L, what is the initial volume of the ideal gas?
39. An ideal gas is carried through a thermodynamic cycle consisting of two isobaric and two isothermal processes, as shown in Figure P20.39. Show that the net work done in the entire cycle is given by the equation

$$W_{\text{net}} = P_1(V_2 - V_1) \ln \frac{P_2}{P_1}$$

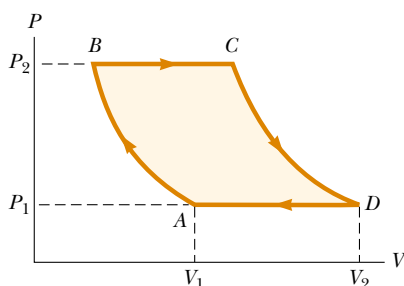


Figure P20.39

40. In Figure P20.40, the change in internal energy of a gas that is taken from A to C is +800 J. The work done along the path ABC is +500 J. (a) How much energy must be added to the system by heat as it goes from A through B and on to C? (b) If the pressure at point A is five times that at point C, what is the work done by the system in going from C to D? (c) What is the energy exchanged with the surroundings by heat as the gas is taken from C to A along the green path? (d) If the change in internal energy in going from point D to point A is +500 J, how much energy must be added to the system by heat as it goes from point C to point D?

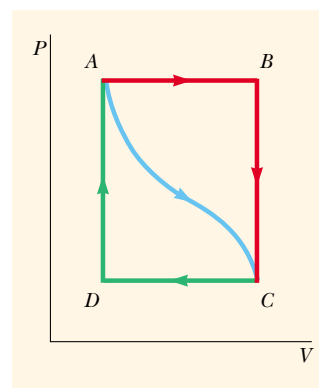


Figure P20.40

- How much energy is lost every second by heat when the steam is at 200°C and the surrounding air is at 20.0°C? The pipe has a circumference of 20.0 cm and a length of 50.0 m. Neglect losses through the ends of the pipe.
42. A box with a total surface area of 1.20 m² and a wall thickness of 4.00 cm is made of an insulating material. A 10.0-W electric heater inside the box maintains the inside temperature at 15.0°C above the outside temperature. Find the thermal conductivity k of the insulating material.
43. A glass window pane has an area of 3.00 m² and a thickness of 0.600 cm. If the temperature difference between its surfaces is 25.0°C, what is the rate of energy transfer by conduction through the window?
44. A thermal window with an area of 6.00 m² is constructed of two layers of glass, each 4.00 mm thick and separated from each other by an air space of 5.00 mm. If the inside surface is at 20.0°C and the outside is at -30.0°C, what is the rate of energy transfer by conduction through the window?
45. A bar of gold is in thermal contact with a bar of silver of the same length and area (Fig. P20.45). One end of the compound bar is maintained at 80.0°C, while the opposite end is at 30.0°C. When the rate of energy transfer by conduction reaches steady state, what is the temperature at the junction?

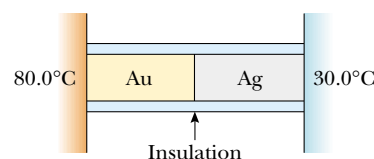


Figure P20.45

Section 20.7 Energy Transfer Mechanisms

41. A steam pipe is covered with 1.50-cm-thick insulating material with a thermal conductivity of 0.200 cal/cm · °C · s.

46. Two rods of the same length but made of different materials and having different cross-sectional areas are placed side by side, as shown in Figure P20.46. Deter-

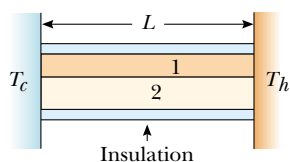


Figure P20.46

mine the rate of energy transfer by conduction in terms of the thermal conductivity and the area of each rod. Generalize your result to a system consisting of several rods.

47. Calculate the R value of (a) a window made of a single pane of flat glass $\frac{1}{8}$ in. thick; (b) a thermal window made of two single panes, each $\frac{1}{8}$ in. thick and separated by a $\frac{1}{4}$ -in. air space. (c) By what factor is the thermal conduction reduced if the thermal window replaces the single-pane window?
48. The surface of the Sun has a temperature of about 5 800 K. The radius of the Sun is 6.96×10^8 m. Calculate the total energy radiated by the Sun each second. (Assume that $e = 0.965$.)
49. A large, hot pizza floats in outer space. What is the order of magnitude (a) of its rate of energy loss? (b) of its rate of temperature change? List the quantities you estimate and the value you estimate for each.
50. The tungsten filament of a certain 100-W light bulb radiates 2.00 W of light. (The other 98 W is carried away by convection and conduction.) The filament has a surface area of 0.250 mm^2 and an emissivity of 0.950. Find the filament's temperature. (The melting point of tungsten is 3 683 K.)
51. At high noon, the Sun delivers 1 000 W to each square meter of a blacktop road. If the hot asphalt loses energy only by radiation, what is its equilibrium temperature?
52. At our distance from the Sun, the intensity of solar radiation is $1\,340 \text{ W/m}^2$. The temperature of the Earth is affected by the so-called "greenhouse effect" of the atmosphere. This effect makes our planet's emissivity for visible light higher than its emissivity for infrared light. For comparison, consider a spherical object with no atmosphere at the same distance from the Sun as the Earth. Assume that its emissivity is the same for all kinds of electromagnetic waves and that its temperature is uniform over its surface. Identify the projected area over which it absorbs sunlight and the surface area over which it radiates. Compute its equilibrium temperature. Chilly, isn't it? Your calculation applies to (a) the average temperature of the Moon, (b) astronauts in mortal danger aboard the crippled *Apollo 13* spacecraft, and (c) global catastrophe on the Earth if widespread fires caused a layer of soot to accumulate throughout the upper atmosphere so that most of the radiation from the Sun was absorbed there rather than at the surface below the atmosphere.

ADDITIONAL PROBLEMS

53. One hundred grams of liquid nitrogen at 77.3 K is stirred into a beaker containing 200 g of water at 5.00°C . If the nitrogen leaves the solution as soon as it turns to gas, how much water freezes? (The latent heat of vaporization of nitrogen is 48.0 cal/g , and the latent heat of fusion of water is 79.6 cal/g .)
54. A 75.0-kg cross-country skier moves across the snow (Fig. P20.54). The coefficient of friction between the skis and the snow is 0.200. Assume that all the snow beneath his skis is at 0°C and that all the internal energy generated by friction is added to the snow, which sticks to his skis until it melts. How far would he have to ski to melt 1.00 kg of snow?



Figure P20.54 A cross-country skier. (Nathan Bilow/Leo de Wys, Inc.)

55. An aluminum rod 0.500 m in length and with a cross-sectional area 2.50 cm^2 is inserted into a thermally insulated vessel containing liquid helium at 4.20 K. The rod is initially at 300 K. (a) If one half of the rod is inserted into the helium, how many liters of helium boil off by the time the inserted half cools to 4.20 K? (Assume that the upper half does not yet cool.) (b) If the upper end of the rod is maintained at 300 K, what is the approximate boil-off rate of liquid helium after the lower half has reached 4.20 K? (Aluminum has thermal conductivity of $31.0 \text{ J/s} \cdot \text{cm} \cdot \text{K}$ at 4.2 K; ignore its temperature variation. Aluminum has a specific heat of $0.210 \text{ cal/g} \cdot ^\circ\text{C}$ and density of 2.70 g/cm^3 . The density of liquid helium is 0.125 g/cm^3 .)
56. On a cold winter day, you buy a hot dog from a street vendor. Into the pocket of your down parka you put the change he gives you: coins consisting of 9.00 g of copper at -12.0°C . Your pocket already contains 14.0 g of silver coins at 30.0°C . A short time later, the temperature of the copper coins is 4.00°C and is increasing at a rate of 0.500°C/s . At this time (a) what is the temperature of the silver coins, and (b) at what rate is it changing? (Neglect energy transferred to the surroundings.)

57. A *flow calorimeter* is an apparatus used to measure the specific heat of a liquid. The technique of flow calorimetry involves measuring the temperature difference between the input and output points of a flowing stream of the liquid while energy is added by heat at a known rate. In one particular experiment, a liquid with a density of 0.780 g/cm^3 flows through the calorimeter at the rate of $4.00 \text{ cm}^3/\text{s}$. At steady state, a temperature difference of 4.80°C is established between the input and output points when energy is supplied by heat at the rate of 30.0 J/s . What is the specific heat of the liquid?

58. A *flow calorimeter* is an apparatus used to measure the specific heat of a liquid. The technique of flow calorimetry involves measuring the temperature difference between the input and output points of a flowing stream of the liquid while energy is added by heat at a known rate. In one particular experiment, a liquid of density ρ flows through the calorimeter with volume flow rate R . At steady state, a temperature difference ΔT is established between the input and output points when energy is supplied at the rate \mathcal{P} . What is the specific heat of the liquid?

59. One mole of an ideal gas, initially at 300 K , is cooled at constant volume so that the final pressure is one-fourth the initial pressure. The gas then expands at constant pressure until it reaches the initial temperature. Determine the work done by the gas.

60. One mole of an ideal gas is contained in a cylinder with a movable piston. The initial pressure, volume, and temperature are P_i , V_i , and T_i , respectively. Find the work done by the gas for the following processes and show each process on a PV diagram: (a) An isobaric compression in which the final volume is one-half the initial volume. (b) An isothermal compression in which the final pressure is four times the initial pressure. (c) An isovolumetric process in which the final pressure is triple the initial pressure.

61. An ideal gas initially at P_i , V_i , and T_i is taken through a cycle as shown in Figure P20.61. (a) Find the net work done by the gas per cycle. (b) What is the net energy added by heat to the system per cycle? (c) Obtain a nu-

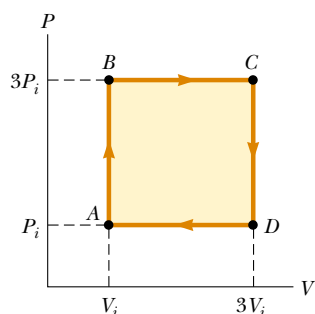


Figure P20.61

merical value for the net work done per cycle for 1.00 mol of gas initially at 0°C .

62. **Review Problem.** An iron plate is held against an iron wheel so that a sliding frictional force of 50.0 N acts between the two pieces of metal. The relative speed at which the two surfaces slide over each other is 40.0 m/s . (a) Calculate the rate at which mechanical energy is converted to internal energy. (b) The plate and the wheel each have a mass of 5.00 kg , and each receives 50.0% of the internal energy. If the system is run as described for 10.0 s and each object is then allowed to reach a uniform internal temperature, what is the resultant temperature increase?

WEB 63. A “solar cooker” consists of a curved reflecting mirror that focuses sunlight onto the object to be warmed (Fig. P20.63). The solar power per unit area reaching the Earth at the location is 600 W/m^2 , and the cooker has a diameter of 0.600 m . Assuming that 40.0% of the incident energy is transferred to the water, how long does it take to completely boil off 0.500 L of water initially at 20.0°C ? (Neglect the heat capacity of the container.)

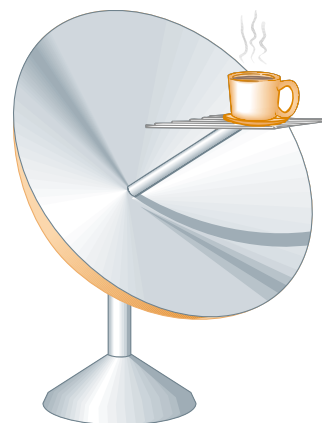


Figure P20.63

64. Water in an electric teakettle is boiling. The power absorbed by the water is 1.00 kW . Assuming that the pressure of the vapor in the kettle equals atmospheric pressure, determine the speed of effusion of vapor from the kettle’s spout if the spout has a cross-sectional area of 2.00 cm^2 .

65. Liquid water evaporates and even boils at temperatures other than 100°C , depending on the ambient pressure. Suppose that the latent heat of vaporization in Table 20.2 describes the liquid–vapor transition at all temperatures. A chamber contains 1.00 kg of water at 0°C under a piston, which just touches the water’s surface. The piston is then raised quickly so that part of the water is vaporized and the other part is frozen (no liquid remains). Assuming that the temperature remains con-

stant at 0°C , determine the mass of the ice that forms in the chamber.

66. A cooking vessel on a slow burner contains 10.0 kg of water and an unknown mass of ice in equilibrium at 0°C at time $t = 0$. The temperature of the mixture is measured at various times, and the result is plotted in Figure P20.66. During the first 50.0 min, the mixture remains at 0°C . From 50.0 min to 60.0 min, the temperature increases to 2.00°C . Neglecting the heat capacity of the vessel, determine the initial mass of the ice.

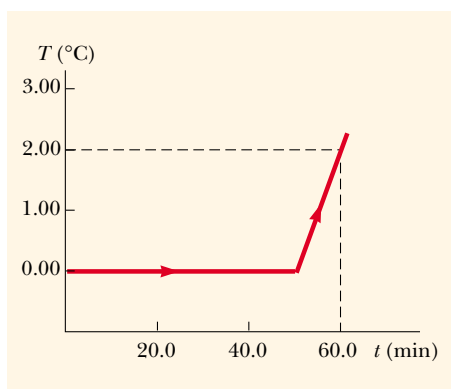


Figure P20.66

67. **Review Problem.** (a) In air at 0°C , a 1.60-kg copper block at 0°C is set sliding at 2.50 m/s over a sheet of ice at 0°C . Friction brings the block to rest. Find the mass of the ice that melts. To describe the process of slowing down, identify the energy input Q , the work output W , the change in internal energy ΔE_{int} , and the change in mechanical energy ΔK for both the block and the ice. (b) A 1.60-kg block of ice at 0°C is set sliding at 2.50 m/s over a sheet of copper at 0°C . Friction brings the block to rest. Find the mass of the ice that melts. Identify Q , W , ΔE_{int} , and ΔK for the block and for the metal sheet during the process. (c) A thin 1.60-kg slab of copper at 20°C is set sliding at 2.50 m/s over an identical stationary slab at the same temperature. Friction quickly stops the motion. If no energy is lost to the environment by heat, find the change in temperature of both objects. Identify Q , W , ΔE_{int} , and ΔK for each object during the process.
68. The average thermal conductivity of the walls (including the windows) and roof of the house depicted in Figure P20.68 is $0.480 \text{ W/m} \cdot ^\circ\text{C}$, and their average thickness is 21.0 cm. The house is heated with natural gas having a heat of combustion (that is, the energy provided per cubic meter of gas burned) of $9\,300 \text{ kcal/m}^3$. How many cubic meters of gas must be burned each day to maintain an inside temperature of 25.0°C if the out-

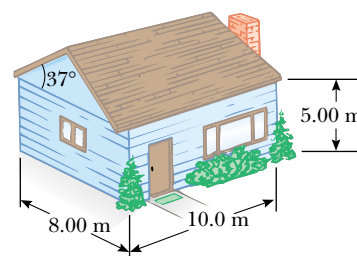


Figure P20.68

side temperature is 0.0°C ? Disregard radiation and the energy lost by heat through the ground.

69. A pond of water at 0°C is covered with a layer of ice 4.00 cm thick. If the air temperature stays constant at -10.0°C , how long does it take the ice's thickness to increase to 8.00 cm? (*Hint:* To solve this problem, use Equation 20.14 in the form

$$\frac{dQ}{dt} = kA \frac{\Delta T}{x}$$

and note that the incremental energy dQ extracted from the water through the thickness x of ice is the amount required to freeze a thickness dx of ice. That is, $dQ = L\rho A dx$, where ρ is the density of the ice, A is the area, and L is the latent heat of fusion.)

70. The inside of a hollow cylinder is maintained at a temperature T_a while the outside is at a lower temperature T_b (Fig. P20.70). The wall of the cylinder has a thermal conductivity k . Neglecting end effects, show that the rate of energy conduction from the inner to the outer wall in the radial direction is

$$\frac{dQ}{dt} = 2\pi Lk \left[\frac{T_a - T_b}{\ln(b/a)} \right]$$

(*Hint:* The temperature gradient is dT/dr . Note that a radial flow of energy occurs through a concentric cylinder of area $2\pi rL$.)

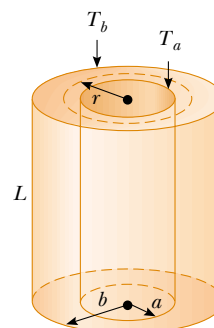


Figure P20.70

- 71.** The passenger section of a jet airliner has the shape of a cylindrical tube with a length of 35.0 m and an inner radius of 2.50 m. Its walls are lined with an insulating material 6.00 cm in thickness and having a thermal conductivity of $4.00 \times 10^{-5} \text{ cal/s} \cdot \text{cm} \cdot ^\circ\text{C}$. A heater must maintain the interior temperature at 25.0°C while the outside temperature is at -35.0°C . What power must be supplied to the heater if this temperature difference is to be maintained? (Use the result you obtained in Problem 70.)
- 72.** A student obtains the following data in a calorimetry experiment designed to measure the specific heat of aluminum:

Initial temperature of water and calorimeter	70°C
Mass of water	0.400 kg
Mass of calorimeter	0.040 kg
Specific heat of calorimeter	$0.63 \text{ kJ/kg} \cdot ^\circ\text{C}$
Initial temperature of aluminum	27°C
Mass of aluminum	0.200 kg
Final temperature of mixture	66.3°C

Use these data to determine the specific heat of aluminum. Your result should be within 15% of the value listed in Table 20.1.

ANSWERS TO QUICK QUIZZES

- 20.1** (a) Water, glass, iron. Because water has the highest specific heat ($4186 \text{ J/kg} \cdot ^\circ\text{C}$), it has the smallest change in temperature. Glass is next ($837 \text{ J/kg} \cdot ^\circ\text{C}$), and iron is last ($448 \text{ J/kg} \cdot ^\circ\text{C}$). (b) Iron, glass, water. For a given temperature increase, the energy transfer by heat is proportional to the specific heat.
- 20.2** Steam. According to Table 20.2, a kilogram of 100°C steam releases $2.26 \times 10^6 \text{ J}$ of energy as it condenses to 100°C water. After it releases this much energy into your skin, it is identical to 100°C water and will continue to burn you.
- 20.3** C, A, E. The slope is the ratio of the temperature change to the amount of energy input. Thus, the slope is proportional to the reciprocal of the specific heat. Water, which has the highest specific heat, has the least slope.
- 20.4**

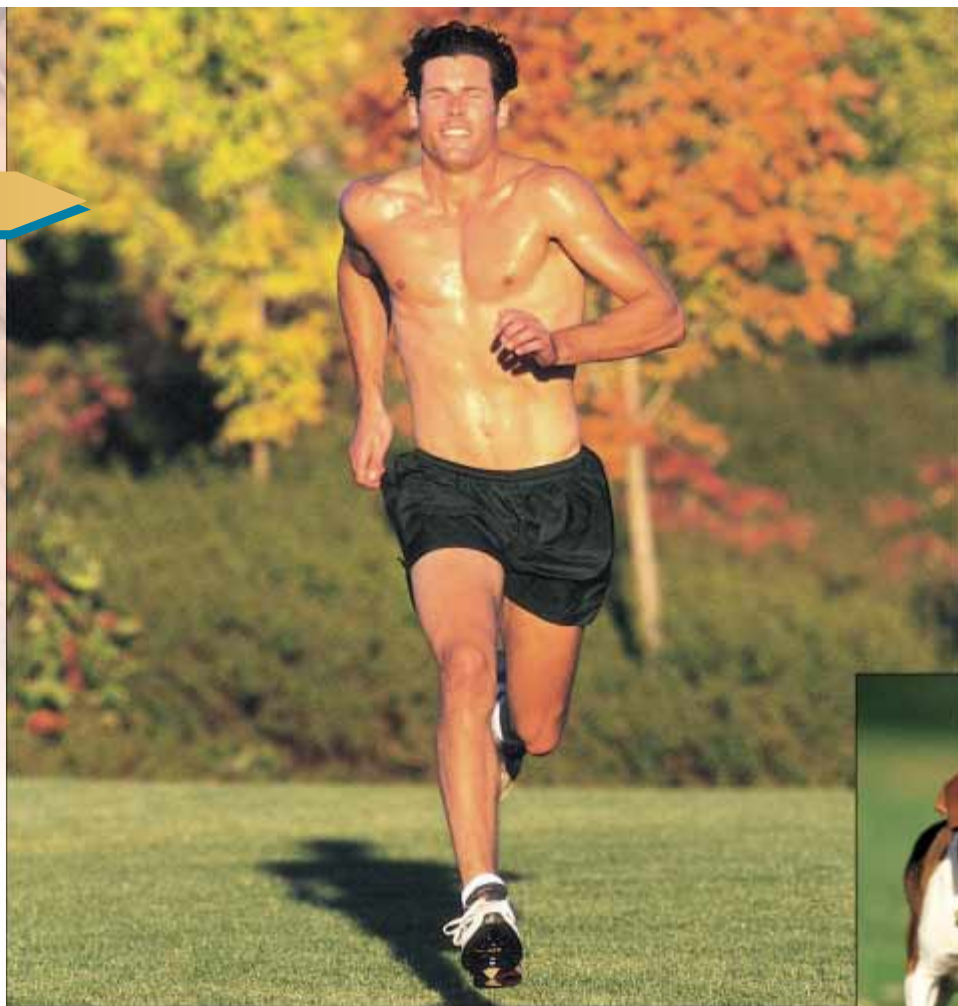
Situation	System	Q	W	ΔE_{int}
(a) Rapidly pumping up a bicycle tire	Air in the pump	0	–	+
(b) Pan of room-temperature water sitting on a hot stove	Water in the pan	+	0	+
(c) Air quickly leaking out of a balloon	Air originally in the balloon	0	+	–

- (a) Because the pumping is rapid, no energy enters or leaves the system by heat; thus, $Q = 0$. Because work is done *on* the system, this work is negative. Thus, $\Delta E_{\text{int}} = Q - W$ must be positive. The air in the pump is warmer. (b) No work is done either by or on the system, but energy flows into the water by heat from the hot burner, making both Q and ΔE_{int} positive. (c) Because the leak is rapid, no energy flows into or out of the system by heat; hence, $Q = 0$. The air molecules escaping from the balloon do work on the surrounding air molecules as they push them out of the way. Thus, W is positive and ΔE_{int} is negative. The decrease in internal energy is evidenced by the fact that the escaping air becomes cooler.
- 20.5** A is isovolumetric, B is adiabatic, C is isothermal, and D is isobaric.
- 20.6** c. The blanket acts as a thermal insulator, slowing the transfer of energy by heat from the air into the cube.

PUZZLER

During periods of strenuous exertion, our bodies generate excess internal energy that must be released into our surroundings. To facilitate this release, humans perspire. Dogs and other animals pant to accomplish the same goal. Both actions involve the evaporation of a liquid. How does this process help cool the body?

(Photograph of runner by Jim Cummins/FPG International; photograph of beagle by Renee Lynn/Photo Researchers, Inc.)



chapter

21

The Kinetic Theory of Gases


Chapter Outline

- | | |
|--|--|
| 21.1 Molecular Model of an Ideal Gas | 21.6 Distribution of Molecular Speeds |
| 21.2 Molar Specific Heat of an Ideal Gas | 21.7 (Optional) Mean Free Path |
| 21.3 Adiabatic Processes for an Ideal Gas | |
| 21.4 The Equipartition of Energy | |
| 21.5 The Boltzmann Distribution Law | |

In Chapter 19 we discussed the properties of an ideal gas, using such macroscopic variables as pressure, volume, and temperature. We shall now show that such large-scale properties can be described on a microscopic scale, where matter is treated as a collection of molecules. Newton's laws of motion applied in a statistical manner to a collection of particles provide a reasonable description of thermodynamic processes. To keep the mathematics relatively simple, we shall consider molecular behavior of gases only, because in gases the interactions between molecules are much weaker than they are in liquids or solids. In the current view of gas behavior, called the *kinetic theory*, gas molecules move about in a random fashion, colliding with the walls of their container and with each other. Perhaps the most important feature of this theory is that it demonstrates that the kinetic energy of molecular motion and the internal energy of a gas system are equivalent. Furthermore, the kinetic theory provides us with a physical basis for our understanding of the concept of temperature.

In the simplest model of a gas, each molecule is considered to be a hard sphere that collides elastically with other molecules and with the container's walls. The hard-sphere model assumes that the molecules do not interact with each other except during collisions and that they are not deformed by collisions. This description is adequate only for monatomic gases, for which the energy is entirely translational kinetic energy. One must modify the theory for more complex molecules, such as oxygen (O_2) and carbon dioxide (CO_2), to include the internal energy associated with rotations and vibrations of the molecules.

21.1 MOLECULAR MODEL OF AN IDEAL GAS

 We begin this chapter by developing a microscopic model of an ideal gas. The model shows that the pressure that a gas exerts on the walls of its container is a consequence of the collisions of the gas molecules with the walls. As we shall see, the model is consistent with the macroscopic description of Chapter 19. In developing this model, we make the following assumptions:

- The number of molecules is large, and the average separation between molecules is great compared with their dimensions. This means that the volume of the molecules is negligible when compared with the volume of the container.
- The molecules obey Newton's laws of motion, but as a whole they move randomly. By "randomly" we mean that any molecule can move in any direction with equal probability. We also assume that the distribution of speeds does not change in time, despite the collisions between molecules. That is, at any given moment, a certain percentage of molecules move at high speeds, a certain percentage move at low speeds, and a certain percentage move at speeds intermediate between high and low.
- The molecules undergo elastic collisions with each other and with the walls of the container. Thus, in the collisions, both kinetic energy and momentum are constant.
- The forces between molecules are negligible except during a collision. The forces between molecules are short-range, so the molecules interact with each other only during collisions.
- The gas under consideration is a pure substance. That is, all of its molecules are identical.

Assumptions of the molecular model of an ideal gas

Although we often picture an ideal gas as consisting of single atoms, we can assume that the behavior of molecular gases approximates that of ideal gases rather

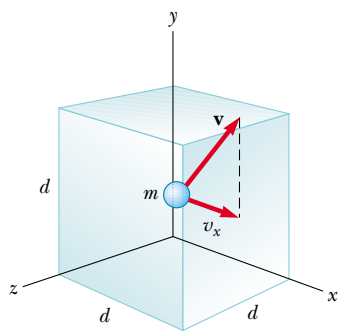


Figure 21.1 A cubical box with sides of length d containing an ideal gas. The molecule shown moves with velocity \mathbf{v} .

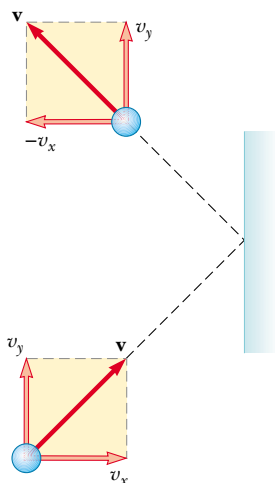


Figure 21.2 A molecule makes an elastic collision with the wall of the container. Its x component of momentum is reversed, while its y component remains unchanged. In this construction, we assume that the molecule moves in the xy plane.

well at low pressures. Molecular rotations or vibrations have no effect, on the average, on the motions that we considered here.

Now let us derive an expression for the pressure of an ideal gas consisting of N molecules in a container of volume V . The container is a cube with edges of length d (Fig. 21.1). Consider the collision of one molecule moving with a velocity \mathbf{v} toward the right-hand face of the box. The molecule has velocity components v_x , v_y , and v_z . Previously, we used m to represent the mass of a sample, but throughout this chapter we shall use m to represent the mass of one molecule. As the molecule collides with the wall elastically, its x component of velocity is reversed, while its y and z components of velocity remain unaltered (Fig. 21.2). Because the x component of the momentum of the molecule is mv_x before the collision and $-mv_x$ after the collision, the change in momentum of the molecule is

$$\Delta p_x = -mv_x - (mv_x) = -2mv_x$$

Applying the impulse–momentum theorem (Eq. 9.9) to the molecule gives

$$F_1 \Delta t = \Delta p_x = -2mv_x$$

where F_1 is the magnitude of the average force exerted by the wall on the molecule in the time Δt . The subscript 1 indicates that we are currently considering only *one* molecule. For the molecule to collide twice with the same wall, it must travel a distance $2d$ in the x direction. Therefore, the time interval between two collisions with the same wall is $\Delta t = 2d/v_x$. Over a time interval that is long compared with Δt , the average force exerted on the molecule for each collision is

$$F_1 = \frac{-2mv_x}{\Delta t} = \frac{-2mv_x}{2d/v_x} = \frac{-mv_x^2}{d} \quad (21.1)$$

According to Newton's third law, the average force exerted by the molecule on the wall is equal in magnitude and opposite in direction to the force in Equation 21.1:

$$F_{1, \text{ on wall}} = -F_1 = -\left(\frac{-mv_x^2}{d}\right) = \frac{mv_x^2}{d}$$

Each molecule of the gas exerts a force F_1 on the wall. We find the total force F exerted by all the molecules on the wall by adding the forces exerted by the individual molecules:

$$F = \frac{m}{d} (v_{x1}^2 + v_{x2}^2 + \cdots)$$

In this equation, v_{x1} is the x component of velocity of molecule 1, v_{x2} is the x component of velocity of molecule 2, and so on. The summation terminates when we reach N molecules because there are N molecules in the container.

To proceed further, we must note that the average value of the square of the velocity in the x direction for N molecules is

$$\overline{v_x^2} = \frac{v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2}{N}$$

Thus, the total force exerted on the wall can be written

$$F = \frac{Nm}{d} \overline{v_x^2}$$

Now let us focus on one molecule in the container whose velocity components are v_x , v_y , and v_z . The Pythagorean theorem relates the square of the speed of this

molecule to the squares of these components:

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

Hence, the average value of v^2 for all the molecules in the container is related to the average values of v_x^2 , v_y^2 , and v_z^2 according to the expression

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

Because the motion is completely random, the average values $\overline{v_x^2}$, $\overline{v_y^2}$, and $\overline{v_z^2}$ are equal to each other. Using this fact and the previous equation, we find that

$$\overline{v^2} = 3\overline{v_x^2}$$

Thus, the total force exerted on the wall is

$$F = \frac{N}{3} \left(\frac{m\overline{v^2}}{d} \right)$$

Using this expression, we can find the total pressure exerted on the wall:


$$P = \frac{F}{A} = \frac{F}{d^2} = \frac{1}{3} \left(\frac{N}{d^3} m\overline{v^2} \right) = \frac{1}{3} \left(\frac{N}{V} \right) m\overline{v^2}$$

$$P = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} m\overline{v^2} \right) \quad (21.2)$$

This result indicates that **the pressure is proportional to the number of molecules per unit volume and to the average translational kinetic energy of the molecules, $\frac{1}{2}m\overline{v^2}$** . In deriving this simplified model of an ideal gas, we obtain an important result that relates the large-scale quantity of pressure to an atomic quantity—the average value of the square of the molecular speed. Thus, we have established a key link between the atomic world and the large-scale world.

You should note that Equation 21.2 verifies some features of pressure with which you are probably familiar. One way to increase the pressure inside a container is to increase the number of molecules per unit volume in the container. This is what you do when you add air to a tire. The pressure in the tire can also be increased by increasing the average translational kinetic energy of the air molecules in the tire. As we shall soon see, this can be accomplished by increasing the temperature of that air. It is for this reason that the pressure inside a tire increases as the tire warms up during long trips. The continuous flexing of the tire as it moves along the surface of a road results in work done as parts of the tire distort and in an increase in internal energy of the rubber. The increased temperature of the rubber results in the transfer of energy by heat into the air inside the tire. This transfer increases the air's temperature, and this increase in temperature in turn produces an increase in pressure.

Molecular Interpretation of Temperature

 We can gain some insight into the meaning of temperature by first writing Equation 21.2 in the more familiar form

$$PV = \frac{2}{3} N \left(\frac{1}{2} m\overline{v^2} \right)$$

Let us now compare this with the equation of state for an ideal gas (Eq. 19.10):

$$PV = Nk_B T$$



Ludwig Boltzmann Austrian theoretical physicist (1844–1906)

Boltzmann made many important contributions to the development of the kinetic theory of gases, electromagnetism, and thermodynamics. His pioneering work in the field of kinetic theory led to the branch of physics known as *statistical mechanics*.

(Courtesy of AIP Niels Bohr Library, Lande Collection)

Relationship between pressure and molecular kinetic energy

Recall that the equation of state is based on experimental facts concerning the macroscopic behavior of gases. Equating the right sides of these expressions, we find that

Temperature is proportional to average kinetic energy

$$T = \frac{2}{3k_B} \left(\frac{1}{2} m \overline{v^2} \right) \quad (21.3)$$

That is, **temperature is a direct measure of average molecular kinetic energy.**

By rearranging Equation 21.3, we can relate the translational molecular kinetic energy to the temperature:

Average kinetic energy per molecule

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T \quad (21.4)$$

That is, the average translational kinetic energy per molecule is $\frac{3}{2} k_B T$. Because $\frac{v_x^2}{v^2} = \frac{1}{3}$, it follows that

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} k_B T \quad (21.5)$$

In a similar manner, it follows that the motions in the y and z directions give us

$$\frac{1}{2} m \overline{v_y^2} = \frac{1}{2} k_B T \quad \text{and} \quad \frac{1}{2} m \overline{v_z^2} = \frac{1}{2} k_B T$$

Thus, each translational degree of freedom contributes an equal amount of energy to the gas, namely, $\frac{1}{2} k_B T$. (In general, “degrees of freedom” refers to the number of independent means by which a molecule can possess energy.) A generalization of this result, known as the **theorem of equipartition of energy**, states that

Theorem of equipartition of energy

each degree of freedom contributes $\frac{1}{2} k_B T$ to the energy of a system.

The total translational kinetic energy of N molecules of gas is simply N times the average energy per molecule, which is given by Equation 21.4:

Total translational kinetic energy of N molecules

$$E_{\text{trans}} = N \left(\frac{1}{2} m \overline{v^2} \right) = \frac{3}{2} N k_B T = \frac{3}{2} n R T \quad (21.6)$$

where we have used $k_B = R/N_A$ for Boltzmann’s constant and $n = N/N_A$ for the number of moles of gas. If we consider a gas for which the only type of energy for the molecules is translational kinetic energy, we can use Equation 21.6 to express

TABLE 21.1 Some rms Speeds

Gas	Molar Mass (g/mol)	v_{rms} at 20°C (m/s)
H ₂	2.02	1904
He	4.00	1352
H ₂ O	18.0	637
Ne	20.2	602
N ₂ or CO	28.0	511
NO	30.0	494
CO ₂	44.0	408
SO ₂	64.1	338

the internal energy of the gas. This result implies that the internal energy of an ideal gas depends only on the temperature.

The square root of $\overline{v^2}$ is called the *root-mean-square (rms) speed* of the molecules. From Equation 21.4 we obtain, for the rms speed,

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}} \quad (21.7)$$

Root-mean-square speed

where M is the molar mass in kilograms per mole. This expression shows that, at a given temperature, lighter molecules move faster, on the average, than do heavier molecules. For example, at a given temperature, hydrogen molecules, whose molar mass is 2×10^{-3} kg/mol, have an average speed four times that of oxygen molecules, whose molar mass is 32×10^{-3} kg/mol. Table 21.1 lists the rms speeds for various molecules at 20°C .

EXAMPLE 21.1 A Tank of Helium

A tank used for filling helium balloons has a volume of 0.300 m^3 and contains 2.00 mol of helium gas at 20.0°C . Assuming that the helium behaves like an ideal gas, (a) what is the total translational kinetic energy of the molecules of the gas?

Solution Using Equation 21.6 with $n = 2.00 \text{ mol}$ and $T = 293 \text{ K}$, we find that

$$\begin{aligned} E_{\text{trans}} &= \frac{3}{2} nRT = \frac{3}{2} (2.00 \text{ mol}) (8.31 \text{ J/mol} \cdot \text{K}) (293 \text{ K}) \\ &= 7.30 \times 10^3 \text{ J} \end{aligned}$$

(b) What is the average kinetic energy per molecule?

Solution Using Equation 21.4, we find that the average kinetic energy per molecule is

$$\begin{aligned} \frac{1}{2} m \overline{v^2} &= \frac{3}{2} k_B T = \frac{3}{2} (1.38 \times 10^{-23} \text{ J/K}) (293 \text{ K}) \\ &= 6.07 \times 10^{-21} \text{ J} \end{aligned}$$

Exercise Using the fact that the molar mass of helium is $4.00 \times 10^{-3} \text{ kg/mol}$, determine the rms speed of the atoms at 20.0°C .

Answer $1.35 \times 10^3 \text{ m/s}$.

Quick Quiz 21.1

At room temperature, the average speed of an air molecule is several hundred meters per second. A molecule traveling at this speed should travel across a room in a small fraction of a second. In view of this, why does it take the odor of perfume (or other smells) several minutes to travel across the room?

21.2 MOLAR SPECIFIC HEAT OF AN IDEAL GAS



10.5

The energy required to raise the temperature of n moles of gas from T_i to T_f depends on the path taken between the initial and final states. To understand this, let us consider an ideal gas undergoing several processes such that the change in temperature is $\Delta T = T_f - T_i$ for all processes. The temperature change can be achieved by taking a variety of paths from one isotherm to another, as shown in Figure 21.3. Because ΔT is the same for each path, the change in internal energy ΔE_{int} is the same for all paths. However, we know from the first law, $Q = \Delta E_{\text{int}} + W$, that the heat Q is different for each path because W (the area under the curves) is different for each path. Thus, the heat associated with a given change in temperature does not have a unique value.

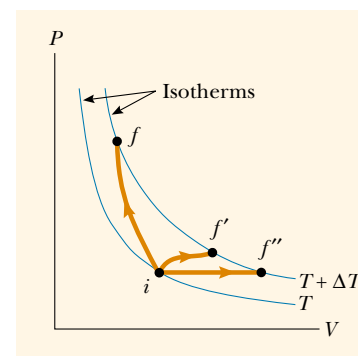


Figure 21.3 An ideal gas is taken from one isotherm at temperature T to another at temperature $T + \Delta T$ along three different paths.

We can address this difficulty by defining specific heats for two processes that frequently occur: changes at constant volume and changes at constant pressure. Because the number of moles is a convenient measure of the amount of gas, we define the **molar specific heats** associated with these processes with the following equations:

$$Q = nC_V\Delta T \quad (\text{constant volume}) \quad (21.8)$$

$$Q = nC_P\Delta T \quad (\text{constant pressure}) \quad (21.9)$$

where C_V is the **molar specific heat at constant volume** and C_P is the **molar specific heat at constant pressure**. When we heat a gas at constant pressure, not only does the internal energy of the gas increase, but the gas also does work because of the change in volume. Therefore, the heat $Q_{\text{constant } P}$ must account for both the increase in internal energy and the transfer of energy out of the system by work, and so $Q_{\text{constant } P}$ is greater than $Q_{\text{constant } V}$. Thus, C_P is greater than C_V .

In the previous section, we found that the temperature of a gas is a measure of the average translational kinetic energy of the gas molecules. This kinetic energy is associated with the motion of the center of mass of each molecule. It does not include the energy associated with the internal motion of the molecule—namely, vibrations and rotations about the center of mass. This should not be surprising because the simple kinetic theory model assumes a structureless molecule.

In view of this, let us first consider the simplest case of an ideal monatomic gas, that is, a gas containing one atom per molecule, such as helium, neon, or argon. When energy is added to a monatomic gas in a container of fixed volume (by heating, for example), all of the added energy goes into increasing the translational kinetic energy of the atoms. There is no other way to store the energy in a monatomic gas. Therefore, from Equation 21.6, we see that the total internal energy E_{int} of N molecules (or n mol) of an ideal monatomic gas is

$$E_{\text{int}} = \frac{3}{2}Nk_B T = \frac{3}{2}nRT \quad (21.10)$$

Note that for a monatomic ideal gas, E_{int} is a function of T only, and the functional relationship is given by Equation 21.10. In general, the internal energy of an ideal gas is a function of T only, and the exact relationship depends on the type of gas, as we shall soon explore.

Internal energy of an ideal monatomic gas is proportional to its temperature

Quick Quiz 21.2

How does the internal energy of a gas change as its pressure is decreased while its volume is increased in such a way that the process follows the isotherm labeled T in Figure 21.4? (a) E_{int} increases. (b) E_{int} decreases. (c) E_{int} stays the same. (d) There is not enough information to determine ΔE_{int} .

If energy is transferred by heat to a system at *constant volume*, then no work is done by the system. That is, $W = \int P dV = 0$ for a constant-volume process. Hence, from the first law of thermodynamics, we see that

$$Q = \Delta E_{\text{int}} \quad (21.11)$$

In other words, all of the energy transferred by heat goes into increasing the internal energy (and temperature) of the system. A constant-volume process from i to f is described in Figure 21.4, where ΔT is the temperature difference between the two isotherms. Substituting the expression for Q given by Equation 21.8 into

Equation 21.11, we obtain

$$\Delta E_{\text{int}} = nC_V \Delta T \quad (21.12)$$

If the molar specific heat is constant, we can express the internal energy of a gas as

$$E_{\text{int}} = nC_V T$$

This equation applies to all ideal gases—to gases having more than one atom per molecule, as well as to monatomic ideal gases.

In the limit of infinitesimal changes, we can use Equation 21.12 to express the molar specific heat at constant volume as

$$C_V = \frac{1}{n} \frac{dE_{\text{int}}}{dT} \quad (21.13)$$

Let us now apply the results of this discussion to the monatomic gas that we have been studying. Substituting the internal energy from Equation 21.10 into Equation 21.13, we find that

$$C_V = \frac{3}{2} R \quad (21.14)$$

This expression predicts a value of $C_V = \frac{3}{2} R = 12.5 \text{ J/mol} \cdot \text{K}$ for all monatomic gases. This is in excellent agreement with measured values of molar specific heats for such gases as helium, neon, argon, and xenon over a wide range of temperatures (Table 21.2).

Now suppose that the gas is taken along the constant-pressure path $i \rightarrow f'$ shown in Figure 21.4. Along this path, the temperature again increases by ΔT . The energy that must be transferred by heat to the gas in this process is $Q = nC_P \Delta T$. Because the volume increases in this process, the work done by the gas is $W = P\Delta V$, where P is the constant pressure at which the process occurs. Applying

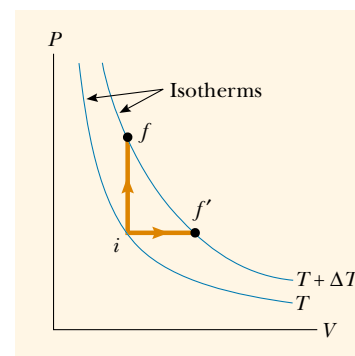


Figure 21.4 Energy is transferred by heat to an ideal gas in two ways. For the constant-volume path $i \rightarrow f$, all the energy goes into increasing the internal energy of the gas because no work is done. Along the constant-pressure path $i \rightarrow f'$, part of the energy transferred in by heat is transferred out by work done by the gas.

TABLE 21.2 Molar Specific Heats of Various Gases

Gas	Molar Specific Heat (J/mol · K) ^a			
	C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
Monatomic Gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic Gases				
H ₂	28.8	20.4	8.33	1.41
N ₂	29.1	20.8	8.33	1.40
O ₂	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl ₂	34.7	25.7	8.96	1.35
Polyatomic Gases				
CO ₂	37.0	28.5	8.50	1.30
SO ₂	40.4	31.4	9.00	1.29
H ₂ O	35.4	27.0	8.37	1.30
CH ₄	35.5	27.1	8.41	1.31

^a All values except that for water were obtained at 300 K.

the first law to this process, we have

$$\Delta E_{\text{int}} = Q - W = nC_P \Delta T - P\Delta V \quad (21.15)$$

In this case, the energy added to the gas by heat is channeled as follows: Part of it does external work (that is, it goes into moving a piston), and the remainder increases the internal energy of the gas. But the change in internal energy for the process $i \rightarrow f'$ is equal to that for the process $i \rightarrow f$ because E_{int} depends only on temperature for an ideal gas and because ΔT is the same for both processes. In addition, because $PV = nRT$, we note that for a constant-pressure process, $P\Delta V = nR\Delta T$. Substituting this value for $P\Delta V$ into Equation 21.15 with $\Delta E_{\text{int}} = nC_V \Delta T$ (Eq. 21.12) gives

$$\begin{aligned} nC_V \Delta T &= nC_P \Delta T - nR\Delta T \\ C_P - C_V &= R \end{aligned} \quad (21.16)$$

This expression applies to *any* ideal gas. It predicts that the molar specific heat of an ideal gas at constant pressure is greater than the molar specific heat at constant volume by an amount R , the universal gas constant (which has the value $8.31 \text{ J/mol} \cdot \text{K}$). This expression is applicable to real gases, as the data in Table 21.2 show.

Because $C_V = \frac{3}{2}R$ for a monatomic ideal gas, Equation 21.16 predicts a value $C_P = \frac{5}{2}R = 20.8 \text{ J/mol} \cdot \text{K}$ for the molar specific heat of a monatomic gas at constant pressure. The ratio of these heat capacities is a dimensionless quantity γ (Greek letter gamma):

Ratio of molar specific heats for a monatomic ideal gas

$$\gamma = \frac{C_P}{C_V} = \frac{(5/2)R}{(3/2)R} = \frac{5}{3} = 1.67 \quad (21.17)$$

Theoretical values of C_P and γ are in excellent agreement with experimental values obtained for monatomic gases, but they are in serious disagreement with the values for the more complex gases (see Table 21.2). This is not surprising because the value $C_V = \frac{3}{2}R$ was derived for a monatomic ideal gas, and we expect some additional contribution to the molar specific heat from the internal structure of the more complex molecules. In Section 21.4, we describe the effect of molecular structure on the molar specific heat of a gas. We shall find that the internal energy—and, hence, the molar specific heat—of a complex gas must include contributions from the rotational and the vibrational motions of the molecule.

We have seen that the molar specific heats of gases at constant pressure are greater than the molar specific heats at constant volume. This difference is a consequence of the fact that in a constant-volume process, no work is done and all of the energy transferred by heat goes into increasing the internal energy (and temperature) of the gas, whereas in a constant-pressure process, some of the energy transferred by heat is transferred out as work done by the gas as it expands. In the case of solids and liquids heated at constant pressure, very little work is done because the thermal expansion is small. Consequently, C_P and C_V are approximately equal for solids and liquids.

EXAMPLE 21.2 Heating a Cylinder of Helium

A cylinder contains 3.00 mol of helium gas at a temperature of 300 K. (a) If the gas is heated at constant volume, how much energy must be transferred by heat to the gas for its temperature to increase to 500 K?

Solution For the constant-volume process, we have

$$Q_1 = nC_V \Delta T$$

Because $C_V = 12.5 \text{ J/mol} \cdot \text{K}$ for helium and $\Delta T = 200 \text{ K}$, we

obtain

$$Q_1 = (3.00 \text{ mol})(12.5 \text{ J/mol} \cdot \text{K})(200 \text{ K}) = 7.50 \times 10^3 \text{ J}$$

$$Q_2 = nC_p \Delta T = (3.00 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(200 \text{ K})$$

$$= 12.5 \times 10^3 \text{ J}$$

(b) How much energy must be transferred by heat to the gas at constant pressure to raise the temperature to 500 K?

Exercise What is the work done by the gas in this isobaric process?

Solution Making use of Table 21.2, we obtain

Answer $W = Q_2 - Q_1 = 5.00 \times 10^3 \text{ J}.$

21.3 ADIABATIC PROCESSES FOR AN IDEAL GAS

As we noted in Section 20.6, an adiabatic process is one in which no energy is transferred by heat between a system and its surroundings. For example, if a gas is compressed (or expanded) very rapidly, very little energy is transferred out of (or into) the system by heat, and so the process is nearly adiabatic. (We must remember that the temperature of a system changes in an adiabatic process even though no energy is transferred by heat.) Such processes occur in the cycle of a gasoline engine, which we discuss in detail in the next chapter.

Another example of an adiabatic process is the very slow expansion of a gas that is thermally insulated from its surroundings. In general,

an **adiabatic process** is one in which no energy is exchanged by heat between a system and its surroundings.

Definition of an adiabatic process

Let us suppose that an ideal gas undergoes an adiabatic expansion. At any time during the process, we assume that the gas is in an equilibrium state, so that the equation of state $PV = nRT$ is valid. As we shall soon see, the pressure and volume at any time during an adiabatic process are related by the expression

$$PV^\gamma = \text{constant} \quad (21.18)$$

Relationship between P and V for an adiabatic process involving an ideal gas

where $\gamma = C_p/C_V$ is assumed to be constant during the process. Thus, we see that all three variables in the ideal gas law— P , V , and T —change during an adiabatic process.

Proof That $PV^\gamma = \text{constant}$ for an Adiabatic Process

When a gas expands adiabatically in a thermally insulated cylinder, no energy is transferred by heat between the gas and its surroundings; thus, $Q = 0$. Let us take the infinitesimal change in volume to be dV and the infinitesimal change in temperature to be dT . The work done by the gas is $P dV$. Because the internal energy of an ideal gas depends only on temperature, the change in the internal energy in an adiabatic expansion is the same as that for an isovolumetric process between the same temperatures, $dE_{\text{int}} = nC_V dT$ (Eq. 21.12). Hence, the first law of thermodynamics, $\Delta E_{\text{int}} = Q - W$, with $Q = 0$, becomes

$$dE_{\text{int}} = nC_V dT = -P dV$$

Taking the total differential of the equation of state of an ideal gas, $PV = nRT$, we

QuickLab

Rapidly pump up a bicycle tire and then feel the coupling at the end of the hose. Why is the coupling warm?

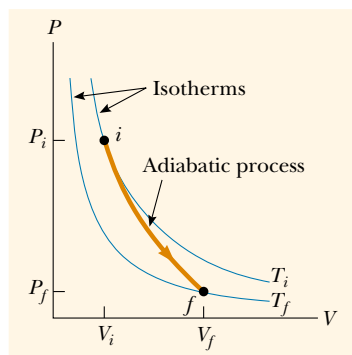


Figure 21.5 The PV diagram for an adiabatic expansion. Note that $T_f < T_i$ in this process.

Adiabatic process

see that

$$P dV + V dP = nR dT$$

Eliminating dT from these two equations, we find that

$$P dV + V dP = -\frac{R}{C_V} P dV$$

Substituting $R = C_P - C_V$ and dividing by PV , we obtain

$$\frac{dV}{V} + \frac{dP}{P} = -\left(\frac{C_P - C_V}{C_V}\right) \frac{dV}{V} = (1 - \gamma) \frac{dV}{V}$$

$$\frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

Integrating this expression, we have

$$\ln P + \gamma \ln V = \text{constant}$$

which is equivalent to Equation 21.18:

$$PV^\gamma = \text{constant}$$

The PV diagram for an adiabatic expansion is shown in Figure 21.5. Because $\gamma > 1$, the PV curve is steeper than it would be for an isothermal expansion. By the definition of an adiabatic process, no energy is transferred by heat into or out of the system. Hence, from the first law, we see that ΔE_{int} is negative (the gas does work, so its internal energy decreases) and so ΔT also is negative. Thus, we see that the gas cools ($T_f < T_i$) during an adiabatic expansion. Conversely, the temperature increases if the gas is compressed adiabatically. Applying Equation 21.18 to the initial and final states, we see that

$$P_i V_i^\gamma = P_f V_f^\gamma \quad (21.19)$$

Using the ideal gas law, we can express Equation 21.19 as

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \quad (21.20)$$

EXAMPLE 21.3 A Diesel Engine Cylinder

Air at 20.0°C in the cylinder of a diesel engine is compressed from an initial pressure of 1.00 atm and volume of 800.0 cm^3 to a volume of 60.0 cm^3 . Assume that air behaves as an ideal gas with $\gamma = 1.40$ and that the compression is adiabatic. Find the final pressure and temperature of the air.

Solution Using Equation 21.19, we find that

$$\begin{aligned} P_f &= P_i \left(\frac{V_i}{V_f} \right)^\gamma = (1.00 \text{ atm}) \left(\frac{800.0 \text{ cm}^3}{60.0 \text{ cm}^3} \right)^{1.40} \\ &= 37.6 \text{ atm} \end{aligned}$$

Because $PV = nRT$ is valid during any process and because

no gas escapes from the cylinder,

$$\begin{aligned} \frac{P_i V_i}{T_i} &= \frac{P_f V_f}{T_f} \\ T_f &= \frac{P_f V_f}{P_i V_i} T_i = \frac{(37.6 \text{ atm})(60.0 \text{ cm}^3)}{(1.00 \text{ atm})(800.0 \text{ cm}^3)} (293 \text{ K}) \\ &= 826 \text{ K} = 553^\circ\text{C} \end{aligned}$$

The high compression in a diesel engine raises the temperature of the fuel enough to cause its combustion without the use of spark plugs.

21.4 THE EQUIPARTITION OF ENERGY

We have found that model predictions based on molar specific heat agree quite well with the behavior of monatomic gases but not with the behavior of complex gases (see Table 21.2). Furthermore, the value predicted by the model for the quantity $C_P - C_V = R$ is the same for all gases. This is not surprising because this difference is the result of the work done by the gas, which is independent of its molecular structure.

To clarify the variations in C_V and C_P in gases more complex than monatomic gases, let us first explain the origin of molar specific heat. So far, we have assumed that the sole contribution to the internal energy of a gas is the translational kinetic energy of the molecules. However, the internal energy of a gas actually includes contributions from the translational, vibrational, and rotational motion of the molecules. The rotational and vibrational motions of molecules can be activated by collisions and therefore are “coupled” to the translational motion of the molecules. The branch of physics known as *statistical mechanics* has shown that, for a large number of particles obeying the laws of Newtonian mechanics, the available energy is, on the average, shared equally by each independent degree of freedom. Recall from Section 21.1 that the equipartition theorem states that, at equilibrium, each degree of freedom contributes $\frac{1}{2}k_B T$ of energy per molecule.

Let us consider a diatomic gas whose molecules have the shape of a dumbbell (Fig. 21.6). In this model, the center of mass of the molecule can translate in the x , y , and z directions (Fig. 21.6a). In addition, the molecule can rotate about three mutually perpendicular axes (Fig. 21.6b). We can neglect the rotation about the y axis because the moment of inertia I_y and the rotational energy $\frac{1}{2}I_y\omega^2$ about this axis are negligible compared with those associated with the x and z axes. (If the two atoms are taken to be point masses, then I_y is identically zero.) Thus, there are five degrees of freedom: three associated with the translational motion and two associated with the rotational motion. Because each degree of freedom contributes, on the average, $\frac{1}{2}k_B T$ of energy per molecule, the total internal energy for a system of N molecules is

$$E_{\text{int}} = 3N(\frac{1}{2}k_B T) + 2N(\frac{1}{2}k_B T) = \frac{5}{2}Nk_B T = \frac{5}{2}nRT$$

We can use this result and Equation 21.13 to find the molar specific heat at constant volume:

$$C_V = \frac{1}{n} \frac{dE_{\text{int}}}{dT} = \frac{1}{n} \frac{d}{dT} \left(\frac{5}{2} nRT \right) = \frac{5}{2} R$$

From Equations 21.16 and 21.17, we find that

$$C_P = C_V + R = \frac{7}{2} R$$

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{7}{2} R}{\frac{5}{2} R} = \frac{7}{5} = 1.40$$

These results agree quite well with most of the data for diatomic molecules given in Table 21.2. This is rather surprising because we have not yet accounted for the possible vibrations of the molecule. In the vibratory model, the two atoms are joined by an imaginary spring (see Fig. 21.6c). The vibrational motion adds two more degrees of freedom, which correspond to the kinetic energy and the potential energy associated with vibrations along the length of the molecule. Hence, classical physics and the equipartition theorem predict an internal energy of

$$E_{\text{int}} = 3N(\frac{1}{2}k_B T) + 2N(\frac{1}{2}k_B T) + 2N(\frac{1}{2}k_B T) = \frac{7}{2}Nk_B T = \frac{7}{2}nRT$$

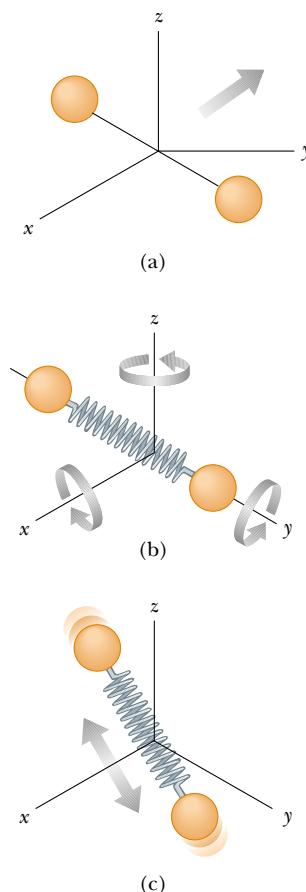


Figure 21.6 Possible motions of a diatomic molecule: (a) translational motion of the center of mass, (b) rotational motion about the various axes, and (c) vibrational motion along the molecular axis.

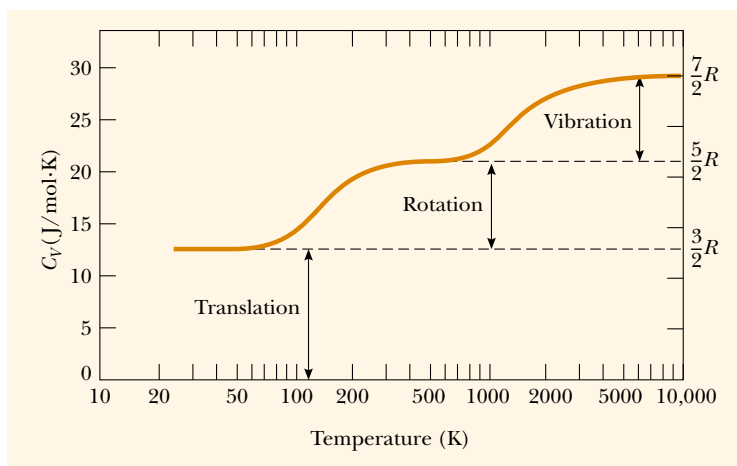


Figure 21.7 The molar specific heat of hydrogen as a function of temperature. The horizontal scale is logarithmic. Note that hydrogen liquefies at 20 K.

and a molar specific heat at constant volume of

$$C_V = \frac{1}{n} \frac{dE_{\text{int}}}{dT} = \frac{1}{n} \frac{d}{dT} \left(\frac{7}{2} nRT \right) = \frac{7}{2} R$$

This value is inconsistent with experimental data for molecules such as H_2 and N_2 (see Table 21.2) and suggests a breakdown of our model based on classical physics.

For molecules consisting of more than two atoms, the number of degrees of freedom is even larger and the vibrations are more complex. This results in an even higher predicted molar specific heat, which is in qualitative agreement with experiment. The more degrees of freedom available to a molecule, the more “ways” it can store internal energy; this results in a higher molar specific heat.

We have seen that the equipartition theorem is successful in explaining some features of the molar specific heat of gas molecules with structure. However, the theorem does not account for the observed temperature variation in molar specific heats. As an example of such a temperature variation, C_V for H_2 is $\frac{5}{2}R$ from about 250 K to 750 K and then increases steadily to about $\frac{7}{2}R$ well above 750 K (Fig. 21.7). This suggests that much more significant vibrations occur at very high temperatures. At temperatures well below 250 K, C_V has a value of about $\frac{3}{2}R$, suggesting that the molecule has only translational energy at low temperatures.

A Hint of Energy Quantization

The failure of the equipartition theorem to explain such phenomena is due to the inadequacy of classical mechanics applied to molecular systems. For a more satisfactory description, it is necessary to use a quantum-mechanical model, in which the energy of an individual molecule is quantized. The energy separation between adjacent vibrational energy levels for a molecule such as H_2 is about ten times greater than the average kinetic energy of the molecule at room temperature. Consequently, collisions between molecules at low temperatures do not provide enough energy to change the vibrational state of the molecule. It is often stated that such degrees of freedom are “frozen out.” This explains why the vibrational energy does not contribute to the molar specific heats of molecules at low temperatures.

The rotational energy levels also are quantized, but their spacing at ordinary temperatures is small compared with $k_B T$. Because the spacing between quantized energy levels is small compared with the available energy, the system behaves in accordance with classical mechanics. However, at sufficiently low temperatures (typically less than 50 K), where $k_B T$ is small compared with the spacing between rotational levels, intermolecular collisions may not be sufficiently energetic to alter the rotational states. This explains why C_V reduces to $\frac{3}{2}R$ for H_2 in the range from 20 K to approximately 100 K.

The Molar Specific Heat of Solids

The molar specific heats of solids also demonstrate a marked temperature dependence. Solids have molar specific heats that generally decrease in a nonlinear manner with decreasing temperature and approach zero as the temperature approaches absolute zero. At high temperatures (usually above 300 K), the molar specific heats approach the value of $3R \approx 25 \text{ J/mol} \cdot \text{K}$, a result known as the *Dulong–Petit law*. The typical data shown in Figure 21.8 demonstrate the temperature dependence of the molar specific heats for two semiconducting solids, silicon and germanium.

We can explain the molar specific heat of a solid at high temperatures using the equipartition theorem. For small displacements of an atom from its equilibrium position, each atom executes simple harmonic motion in the x , y , and z directions. The energy associated with vibrational motion in the x direction is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}kx^2$$

The expressions for vibrational motions in the y and z directions are analogous. Therefore, each atom of the solid has six degrees of freedom. According to the equipartition theorem, this corresponds to an average vibrational energy of $6(\frac{1}{2}k_B T) = 3k_B T$ per atom. Therefore, the total internal energy of a solid consisting of N atoms is

$$E_{\text{int}} = 3Nk_B T = 3nRT \quad (21.21)$$

From this result, we find that the molar specific heat of a solid at constant volume is

$$C_V = \frac{1}{n} \frac{dE_{\text{int}}}{dT} = 3R \quad (21.22)$$

This result is in agreement with the empirical DuLong–Petit law. The discrepancies between this model and the experimental data at low temperatures are again due to the inadequacy of classical physics in describing the microscopic world.

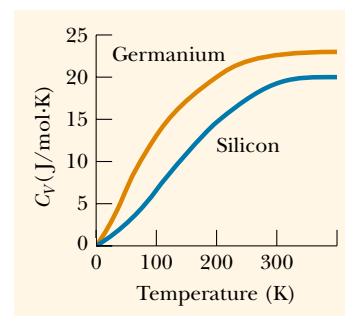


Figure 21.8 Molar specific heat of silicon and germanium. As T approaches zero, the molar specific heat also approaches zero. (From C. Kittel, *Introduction to Solid State Physics*, New York, Wiley, 1971.)

Total internal energy of a solid

Molar specific heat of a solid at constant volume

21.5 THE BOLTZMANN DISTRIBUTION LAW

Thus far we have neglected the fact that not all molecules in a gas have the same speed and energy. In reality, their motion is extremely chaotic. Any individual molecule is colliding with others at an enormous rate—typically, a billion times per second. Each collision results in a change in the speed and direction of motion of each of the participant molecules. From Equation 21.7, we see that average molecular speeds increase with increasing temperature. What we would like to know now is the relative number of molecules that possess some characteristic, such as a certain percentage of the total energy or speed. The ratio of the number of molecules

that have the desired characteristic to the total number of molecules is the probability that a particular molecule has that characteristic.

The Exponential Atmosphere

We begin by considering the distribution of molecules in our atmosphere. Let us determine how the number of molecules per unit volume varies with altitude. Our model assumes that the atmosphere is at a constant temperature T . (This assumption is not entirely correct because the temperature of our atmosphere decreases by about 2°C for every 300-m increase in altitude. However, the model does illustrate the basic features of the distribution.)

According to the ideal gas law, a gas containing N molecules in thermal equilibrium obeys the relationship $PV = Nk_B T$. It is convenient to rewrite this equation in terms of the **number density** $n_V = N/V$, which represents the number of molecules per unit volume of gas. This quantity is important because it can vary from one point to another. In fact, our goal is to determine how n_V changes in our atmosphere. We can express the ideal gas law in terms of n_V as $P = n_V k_B T$. Thus, if the number density n_V is known, we can find the pressure, and vice versa. The pressure in the atmosphere decreases with increasing altitude because a given layer of air must support the weight of all the atmosphere above it—that is, the greater the altitude, the less the weight of the air above that layer, and the lower the pressure.

To determine the variation in pressure with altitude, let us consider an atmospheric layer of thickness dy and cross-sectional area A , as shown in Figure 21.9. Because the air is in static equilibrium, the magnitude PA of the upward force exerted on the bottom of this layer must exceed the magnitude of the downward force on the top of the layer, $(P + dP)A$, by an amount equal to the weight of gas in this thin layer. If the mass of a gas molecule in the layer is m , and if a total of N molecules are in the layer, then the weight of the layer is given by $mgN = mgn_V V = mgn_V A dy$. Thus, we see that

$$PA - (P + dP)A = mgn_V A dy$$

This expression reduces to

$$dP = -mgn_V dy$$

Because $P = n_V k_B T$ and T is assumed to remain constant, we see that $dP = k_B T dn_V$. Substituting this result into the previous expression for dP and rearranging terms, we have

$$\frac{dn_V}{n_V} = -\frac{mg}{k_B T} dy$$

Integrating this expression, we find that

$$n_V(y) = n_0 e^{-mgy/k_B T} \quad (21.23)$$

where the constant n_0 is the number density at $y = 0$. This result is known as the **law of atmospheres**.

According to Equation 21.23, the number density decreases exponentially with increasing altitude when the temperature is constant. The number density of our atmosphere at sea level is about $n_0 = 2.69 \times 10^{25}$ molecules/ m^3 . Because the pressure is $P = n_V k_B T$, we see from Equation 21.23 that the pressure of our atmosphere varies with altitude according to the expression

$$P = P_0 e^{-mgy/k_B T} \quad (21.24)$$

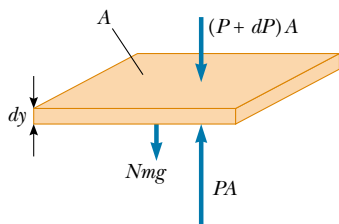


Figure 21.9 An atmospheric layer of gas in equilibrium.

where $P_0 = n_0 k_B T$. A comparison of this model with the actual atmospheric pressure as a function of altitude shows that the exponential form is a reasonable approximation to the Earth's atmosphere.

EXAMPLE 21.4 High-Flying Molecules

What is the number density of air at an altitude of 11.0 km (the cruising altitude of a commercial jetliner) compared with its number density at sea level? Assume that the air temperature at this height is the same as that at the ground, 20°C.

Solution The number density of our atmosphere decreases exponentially with altitude according to the law of atmospheres, Equation 21.23. We assume an average molecular mass of $28.9 \text{ u} = 4.80 \times 10^{-26} \text{ kg}$. Taking $y = 11.0 \text{ km}$, we calculate the power of the exponential in Equation 21.23 to be

$$\frac{mgy}{k_B T} = \frac{(4.80 \times 10^{-26} \text{ kg})(9.80 \text{ m/s}^2)(11\,000 \text{ m})}{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})} = 1.28$$

Thus, Equation 21.23 gives

$$n_V = n_0 e^{-mgy/k_B T} = n_0 e^{-1.28} = 0.278 n_0$$

That is, the number density of air at an altitude of 11.0 km is only 27.8% of the number density at sea level, if we assume constant temperature. Because the temperature actually decreases with altitude, the number density of air is less than this in reality.

The pressure at this height is reduced in the same manner. For this reason, high-flying aircraft must have pressurized cabins to ensure passenger comfort and safety.

Computing Average Values

The exponential function $e^{-mgy/k_B T}$ that appears in Equation 21.23 can be interpreted as a probability distribution that gives the relative probability of finding a gas molecule at some height y . Thus, the probability distribution $p(y)$ is proportional to the number density distribution $n_V(y)$. This concept enables us to determine many properties of the atmosphere, such as the fraction of molecules below a certain height or the average potential energy of a molecule.

As an example, let us determine the average height \bar{y} of a molecule in the atmosphere at temperature T . The expression for this average height is

$$\bar{y} = \frac{\int_0^\infty y n_V(y) dy}{\int_0^\infty n_V(y) dy} = \frac{\int_0^\infty y e^{-mgy/k_B T} dy}{\int_0^\infty e^{-mgy/k_B T} dy}$$

where the height of a molecule can range from 0 to ∞ . The numerator in this expression represents the sum of the heights of the molecules times their number, while the denominator is the sum of the number of molecules. That is, the denominator is the total number of molecules. After performing the indicated integrations, we find that

$$\bar{y} = \frac{(k_B T/mg)^2}{k_B T/mg} = \frac{k_B T}{mg}$$

This expression states that the average height of a molecule increases as T increases, as expected.

We can use a similar procedure to determine the average potential energy of a gas molecule. Because the gravitational potential energy of a molecule at height y is $U = mgy$, the average potential energy is equal to $mg\bar{y}$. Because $\bar{y} = k_B T/mg$, we

see that $\bar{U} = mg(k_B T/mg) = k_B T$. This important result indicates that the average gravitational potential energy of a molecule depends only on temperature, and not on m or g .

The Boltzmann Distribution

Because the gravitational potential energy of a molecule at height y is $U = mgy$, we can express the law of atmospheres (Eq. 21.23) as

$$n_V = n_0 e^{-U/k_B T}$$

This means that gas molecules in thermal equilibrium are distributed in space with a probability that depends on gravitational potential energy according to the exponential factor $e^{-U/k_B T}$.

This exponential expression describing the distribution of molecules in the atmosphere is powerful and applies to any type of energy. In general, the number density of molecules having energy E is

$$n_V(E) = n_0 e^{-E/k_B T} \quad (21.25)$$

This equation is known as the **Boltzmann distribution law** and is important in describing the statistical mechanics of a large number of molecules. It states that **the probability of finding the molecules in a particular energy state varies exponentially as the negative of the energy divided by $k_B T$** . All the molecules would fall into the lowest energy level if the thermal agitation at a temperature T did not excite the molecules to higher energy levels.

Boltzmann distribution law

EXAMPLE 21.5 Thermal Excitation of Atomic Energy Levels

As we discussed briefly in Section 8.10, atoms can occupy only certain discrete energy levels. Consider a gas at a temperature of 2 500 K whose atoms can occupy only two energy levels separated by 1.50 eV, where 1 eV (electron volt) is an energy unit equal to 1.6×10^{-19} J (Fig. 21.10). Determine the ratio of the number of atoms in the higher energy level to the number in the lower energy level.

Solution Equation 21.25 gives the relative number of atoms in a given energy level. In this case, the atom has two possible energies, E_1 and E_2 , where E_1 is the lower energy level. Hence, the ratio of the number of atoms in the higher energy level to the number in the lower energy level is

$$\frac{n_V(E_2)}{n_V(E_1)} = \frac{n_0 e^{-E_2/k_B T}}{n_0 e^{-E_1/k_B T}} = e^{-(E_2 - E_1)/k_B T}$$

In this problem, $E_2 - E_1 = 1.50$ eV, and the denominator of the exponent is

$$\begin{aligned} k_B T &= (1.38 \times 10^{-23} \text{ J/K})(2\,500 \text{ K}) / 1.60 \times 10^{-19} \text{ J/eV} \\ &= 0.216 \text{ eV} \end{aligned}$$

Therefore, the required ratio is

$$\frac{n(E_2)}{n(E_1)} = e^{-1.50 \text{ eV} / 0.216 \text{ eV}} = e^{-6.94} = 9.64 \times 10^{-4}$$

This result indicates that at $T = 2\,500$ K, only a small fraction of the atoms are in the higher energy level. In fact, for every atom in the higher energy level, there are about 1 000 atoms in the lower level. The number of atoms in the higher level increases at even higher temperatures, but the distribution law specifies that at equilibrium there are always more atoms in the lower level than in the higher level.

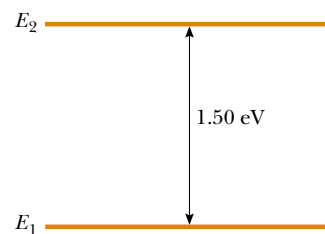


Figure 21.10 Energy level diagram for a gas whose atoms can occupy two energy levels.

21.6 DISTRIBUTION OF MOLECULAR SPEEDS

In 1860 James Clerk Maxwell (1831–1879) derived an expression that describes the distribution of molecular speeds in a very definite manner. His work and subsequent developments by other scientists were highly controversial because direct detection of molecules could not be achieved experimentally at that time. However, about 60 years later, experiments were devised that confirmed Maxwell's predictions.

Let us consider a container of gas whose molecules have some distribution of speeds. Suppose we want to determine how many gas molecules have a speed in the range from, for example, 400 to 410 m/s. Intuitively, we expect that the speed distribution depends on temperature. Furthermore, we expect that the distribution peaks in the vicinity of v_{rms} . That is, few molecules are expected to have speeds much less than or much greater than v_{rms} because these extreme speeds result only from an unlikely chain of collisions.

The observed speed distribution of gas molecules in thermal equilibrium is shown in Figure 21.11. The quantity N_v , called the **Maxwell–Boltzmann distribution function**, is defined as follows: If N is the total number of molecules, then the number of molecules with speeds between v and $v + dv$ is $dN = N_v dv$. This number is also equal to the area of the shaded rectangle in Figure 21.11. Furthermore, the fraction of molecules with speeds between v and $v + dv$ is $N_v dv/N$. This fraction is also equal to the probability that a molecule has a speed in the range v to $v + dv$.

The fundamental expression that describes the distribution of speeds of N gas molecules is

$$N_v = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} \quad (21.26)$$

where m is the mass of a gas molecule, k_B is Boltzmann's constant, and T is the absolute temperature.¹ Observe the appearance of the Boltzmann factor $e^{-E/k_B T}$ with $E = \frac{1}{2}mv^2$.

As indicated in Figure 21.11, the average speed \bar{v} is somewhat lower than the rms speed. The *most probable speed* v_{mp} is the speed at which the distribution curve reaches a peak. Using Equation 21.26, one finds that

$$v_{\text{rms}} = \sqrt{v^2} = \sqrt{3k_B T/m} = 1.73 \sqrt{k_B T/m} \quad (21.27)$$

$$\bar{v} = \sqrt{8k_B T/\pi m} = 1.60 \sqrt{k_B T/m} \quad (21.28)$$

$$v_{\text{mp}} = \sqrt{2k_B T/m} = 1.41 \sqrt{k_B T/m} \quad (21.29)$$

The details of these calculations are left for the student (see Problems 41 and 62). From these equations, we see that

$$v_{\text{rms}} > \bar{v} > v_{\text{mp}}$$

Figure 21.12 represents speed distribution curves for N_2 . The curves were obtained by using Equation 21.26 to evaluate the distribution function at various speeds and at two temperatures. Note that the peak in the curve shifts to the right

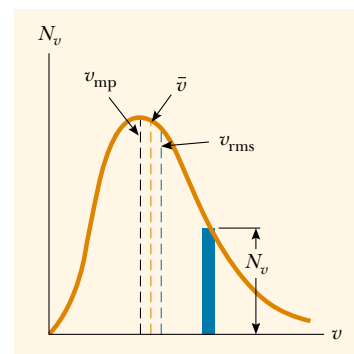


Figure 21.11 The speed distribution of gas molecules at some temperature. The number of molecules having speeds in the range dv is equal to the area of the shaded rectangle, $N_v dv$. The function N_v approaches zero as v approaches infinity.

Maxwell speed distribution function

rms speed

Average speed

Most probable speed

¹ For the derivation of this expression, see an advanced textbook on thermodynamics, such as that by R. P. Bauman, *Modern Thermodynamics with Statistical Mechanics*, New York, Macmillan Publishing Co., 1992.

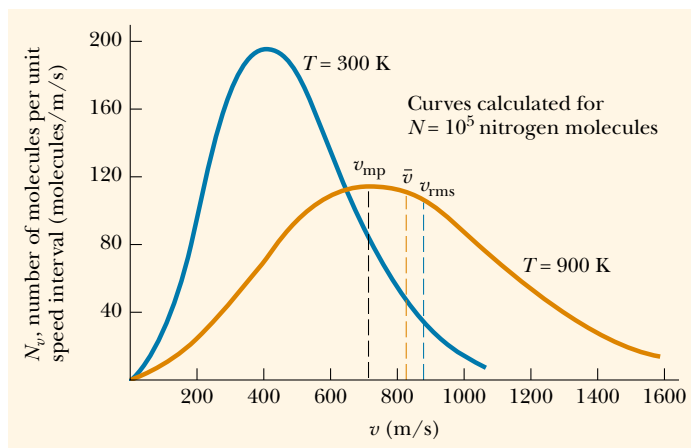


Figure 21.12 The speed distribution function for 10^5 nitrogen molecules at 300 K and 900 K. The total area under either curve is equal to the total number of molecules, which in this case equals 10^5 . Note that $v_{\text{rms}} > \bar{v} > v_{\text{mp}}$.

as T increases, indicating that the average speed increases with increasing temperature, as expected. The asymmetric shape of the curves is due to the fact that the lowest speed possible is zero while the upper classical limit of the speed is infinity.

Quick Quiz 21.3

Consider the two curves in Figure 21.12. What is represented by the area under each of the curves between the 800-m/s and 1 000-m/s marks on the horizontal axis?

QuickLab

Fill one glass with very hot tap water and another with very cold water. Put a single drop of food coloring in each glass. Which drop disperses faster? Why?

Equation 21.26 shows that the distribution of molecular speeds in a gas depends both on mass and on temperature. At a given temperature, the fraction of molecules with speeds exceeding a fixed value increases as the mass decreases. This explains why lighter molecules, such as H_2 and He , escape more readily from the Earth's atmosphere than do heavier molecules, such as N_2 and O_2 . (See the discussion of escape speed in Chapter 14. Gas molecules escape even more readily from the Moon's surface than from the Earth's because the escape speed on the Moon is lower than that on the Earth.)



The speed distribution curves for molecules in a liquid are similar to those shown in Figure 21.12. We can understand the phenomenon of evaporation of a liquid from this distribution in speeds, using the fact that some molecules in the liquid are more energetic than others. Some of the faster-moving molecules in the liquid penetrate the surface and leave the liquid even at temperatures well below the boiling point. The molecules that escape the liquid by evaporation are those that have sufficient energy to overcome the attractive forces of the molecules in the liquid phase. Consequently, the molecules left behind in the liquid phase have a lower average kinetic energy; as a result, the temperature of the liquid decreases. Hence, evaporation is a cooling process. For example, an alcohol-soaked cloth often is placed on a feverish head to cool and comfort a patient.

The evaporation process

EXAMPLE 21.6 A System of Nine Particles

Nine particles have speeds of 5.00, 8.00, 12.0, 12.0, 12.0, 14.0, 14.0, 17.0, and 20.0 m/s. (a) Find the particles' average speed.

Solution The average speed is the sum of the speeds divided by the total number of particles:

$$\bar{v} = \frac{(5.00 + 8.00 + 12.0 + 12.0 + 12.0 + 14.0 + 14.0 + 17.0 + 20.0) \text{ m/s}}{9}$$

$$= 12.7 \text{ m/s}$$

(b) What is the rms speed?

Solution The average value of the square of the speed is

$$\overline{v^2} = \frac{(5.00^2 + 8.00^2 + 12.0^2 + 12.0^2 + 12.0^2 + 14.0^2 + 14.0^2 + 17.0^2 + 20.0^2) \text{ m}^2/\text{s}^2}{9}$$

$$= 178 \text{ m}^2/\text{s}^2$$

Hence, the rms speed is

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{178 \text{ m}^2/\text{s}^2} = 13.3 \text{ m/s}$$

(c) What is the most probable speed of the particles?

Solution Three of the particles have a speed of 12 m/s, two have a speed of 14 m/s, and the remaining have different speeds. Hence, we see that the most probable speed v_{mp} is

12 m/s.

Optional Section**21.7 MEAN FREE PATH**

Most of us are familiar with the fact that the strong odor associated with a gas such as ammonia may take a fraction of a minute to diffuse throughout a room. However, because average molecular speeds are typically several hundred meters per second at room temperature, we might expect a diffusion time much less than 1 s. But, as we saw in Quick Quiz 21.1, molecules collide with one other because they are not geometrical points. Therefore, they do not travel from one side of a room to the other in a straight line. Between collisions, the molecules move with constant speed along straight lines. The average distance between collisions is called the **mean free path**. The path of an individual molecule is random and resembles that shown in Figure 21.13. As we would expect from this description, the mean free path is related to the diameter of the molecules and the density of the gas.

We now describe how to estimate the mean free path for a gas molecule. For this calculation, we assume that the molecules are spheres of diameter d . We see from Figure 21.14a that no two molecules collide unless their centers are less than a distance d apart as they approach each other. An equivalent way to describe the

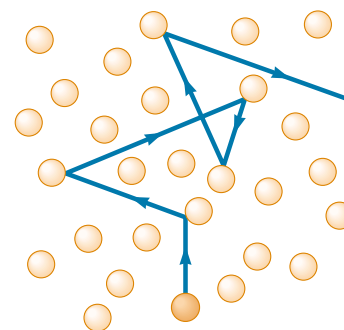


Figure 21.13 A molecule moving through a gas collides with other molecules in a random fashion. This behavior is sometimes referred to as a *random-walk process*. The mean free path increases as the number of molecules per unit volume decreases. Note that the motion is not limited to the plane of the paper.

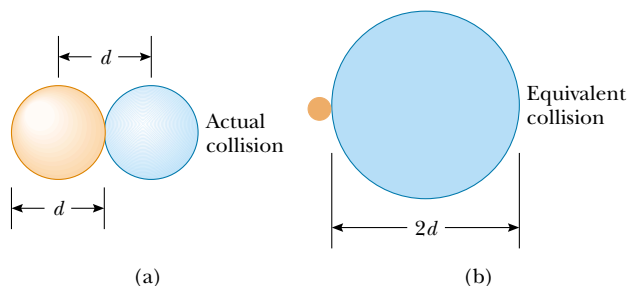


Figure 21.14 (a) Two spherical molecules, each of diameter d , collide if their centers are within a distance d of each other. (b) The collision between the two molecules is equivalent to a point molecule's colliding with a molecule having an effective diameter of $2d$.

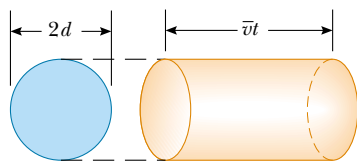


Figure 21.15 In a time t , a molecule of effective diameter $2d$ sweeps out a cylinder of length $\bar{v}t$, where \bar{v} is its average speed. In this time, it collides with every point molecule within this cylinder.

collisions is to imagine that one of the molecules has a diameter $2d$ and that the rest are geometrical points (Fig. 21.14b). Let us choose the large molecule to be one moving with the average speed \bar{v} . In a time t , this molecule travels a distance $\bar{v}t$. In this time interval, the molecule sweeps out a cylinder having a cross-sectional area πd^2 and a length $\bar{v}t$ (Fig. 21.15). Hence, the volume of the cylinder is $\pi d^2 \bar{v}t$. If n_V is the number of molecules per unit volume, then the number of point-size molecules in the cylinder is $(\pi d^2 \bar{v}t) n_V$. The molecule of equivalent diameter $2d$ collides with every molecule in this cylinder in the time t . Hence, the number of collisions in the time t is equal to the number of molecules in the cylinder, $(\pi d^2 \bar{v}t) n_V$.

The mean free path ℓ equals the average distance $\bar{v}t$ traveled in a time t divided by the number of collisions that occur in that time:

$$\ell = \frac{\bar{v}t}{(\pi d^2 \bar{v}t) n_V} = \frac{1}{\pi d^2 n_V}$$

Because the number of collisions in a time t is $(\pi d^2 \bar{v}t) n_V$, the number of collisions per unit time, or **collision frequency** f , is

$$f = \pi d^2 \bar{v} n_V$$

The inverse of the collision frequency is the average time between collisions, known as the **mean free time**.

Our analysis has assumed that molecules in the cylinder are stationary. When the motion of these molecules is included in the calculation, the correct results are

Mean free path

$$\ell = \frac{1}{\sqrt{2} \pi d^2 n_V} \quad (21.30)$$

Collision frequency

$$f = \sqrt{2} \pi d^2 \bar{v} n_V = \frac{\bar{v}}{\ell} \quad (21.31)$$

EXAMPLE 21.7 Bouncing Around in the Air

Approximate the air around you as a collection of nitrogen molecules, each of which has a diameter of 2.00×10^{-10} m.

(a) How far does a typical molecule move before it collides with another molecule?

Solution Assuming that the gas is ideal, we can use the equation $PV = Nk_B T$ to obtain the number of molecules per unit volume under typical room conditions:

$$\begin{aligned} n_V &= \frac{N}{V} = \frac{P}{k_B T} = \frac{1.01 \times 10^5 \text{ N/m}^2}{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})} \\ &= 2.50 \times 10^{25} \text{ molecules/m}^3 \end{aligned}$$

Hence, the mean free path is

$$\begin{aligned} \ell &= \frac{1}{\sqrt{2} \pi d^2 n_V} \\ &= \frac{1}{\sqrt{2} \pi (2.00 \times 10^{-10} \text{ m})^2 (2.50 \times 10^{25} \text{ molecules/m}^3)} \\ &= 2.25 \times 10^{-7} \text{ m} \end{aligned}$$

This value is about 10^3 times greater than the molecular diameter.

(b) On average, how frequently does one molecule collide with another?

Solution Because the rms speed of a nitrogen molecule at 20.0°C is 511 m/s (see Table 21.1), we know from Equations 21.27 and 21.28 that $\bar{v} = (1.60/1.73)(511 \text{ m/s}) = 473 \text{ m/s}$. Therefore, the collision frequency is

$$f = \frac{\bar{v}}{\ell} = \frac{473 \text{ m/s}}{2.25 \times 10^{-7} \text{ m}} = 2.10 \times 10^9/\text{s}$$

The molecule collides with other molecules at the average rate of about two billion times each second!

The mean free path ℓ is *not* the same as the average separation between particles. In fact, the average separation d between particles is approximately $n_V^{-1/3}$. In this example, the average molecular separation is

$$d = \frac{1}{n_V^{1/3}} = \frac{1}{(2.5 \times 10^{25})^{1/3}} = 3.4 \times 10^{-9} \text{ m}$$

SUMMARY

The pressure of N molecules of an ideal gas contained in a volume V is

$$P = \frac{2}{3} \frac{N}{V} \left(\frac{1}{2} m \overline{v^2} \right) \quad (21.2)$$

The average translational kinetic energy per molecule of a gas, $\frac{1}{2} m \overline{v^2}$, is related to the temperature T of the gas through the expression

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T \quad (21.4)$$

where k_B is Boltzmann's constant. Each translational degree of freedom (x , y , or z) has $\frac{1}{2} k_B T$ of energy associated with it.

The **theorem of equipartition of energy** states that the energy of a system in thermal equilibrium is equally divided among all degrees of freedom.

The total energy of N molecules (or n mol) of an ideal monatomic gas is

$$E_{\text{int}} = \frac{3}{2} N k_B T = \frac{3}{2} n R T \quad (21.10)$$

The change in internal energy for n mol of any ideal gas that undergoes a change in temperature ΔT is

$$\Delta E_{\text{int}} = n C_V \Delta T \quad (21.12)$$

where C_V is the molar specific heat at constant volume.

The molar specific heat of an ideal monatomic gas at constant volume is $C_V = \frac{3}{2} R$; the molar specific heat at constant pressure is $C_P = \frac{5}{2} R$. The ratio of specific heats is $\gamma = C_P / C_V = \frac{5}{3}$.

If an ideal gas undergoes an adiabatic expansion or compression, the first law of thermodynamics, together with the equation of state, shows that

$$P V^\gamma = \text{constant} \quad (21.18)$$

The **Boltzmann distribution law** describes the distribution of particles among available energy states. The relative number of particles having energy E is

$$n_V(E) = n_0 e^{-E/k_B T} \quad (21.25)$$

The **Maxwell-Boltzmann distribution function** describes the distribution of speeds of molecules in a gas:

$$N_v = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} \quad (21.26)$$

This expression enables us to calculate the **root-mean-square speed**, the **average speed**, and the **most probable speed**:

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{3k_B T/m} = 1.73 \sqrt{k_B T/m} \quad (21.27)$$

$$\bar{v} = \sqrt{8k_B T/\pi m} = 1.60 \sqrt{k_B T/m} \quad (21.28)$$


$$v_{\text{mp}} = \sqrt{2k_B T/m} = 1.41 \sqrt{k_B T/m} \quad (21.29)$$

QUESTIONS

1. Dalton's law of partial pressures states that the total pressure of a mixture of gases is equal to the sum of the partial pressures of gases making up the mixture. Give a convincing argument for this law on the basis of the kinetic theory of gases.
2. One container is filled with helium gas and another with argon gas. If both containers are at the same temperature, which gas molecules have the higher rms speed? Explain.
3. A gas consists of a mixture of He and N_2 molecules. Do the lighter He molecules travel faster than the N_2 molecules? Explain.
4. Although the average speed of gas molecules in thermal equilibrium at some temperature is greater than zero, the average velocity is zero. Explain why this statement must be true.
5. When alcohol is rubbed on your body, your body temperature decreases. Explain this effect.
6. A liquid partially fills a container. Explain why the temperature of the liquid decreases if the container is then partially evacuated. (Using this technique, one can freeze water at temperatures above 0°C .)
7. A vessel containing a fixed volume of gas is cooled. Does the mean free path of the gas molecules increase, decrease, or remain constant during the cooling process? What about the collision frequency?
8. A gas is compressed at a constant temperature. What happens to the mean free path of the molecules in the process?
9. If a helium-filled balloon initially at room temperature is placed in a freezer, will its volume increase, decrease, or remain the same?
10. What happens to a helium-filled balloon released into the air? Will it expand or contract? Will it stop rising at some height?
11. Which is heavier, dry air or air saturated with water vapor? Explain.
12. Why does a diatomic gas have a greater energy content per mole than a monatomic gas at the same temperature?
13. An ideal gas is contained in a vessel at 300 K. If the temperature is increased to 900 K, (a) by what factor does the rms speed of each molecule change? (b) By what factor does the pressure in the vessel change?
14. A vessel is filled with gas at some equilibrium pressure and temperature. Can all gas molecules in the vessel have the same speed?
15. In our model of the kinetic theory of gases, molecules were viewed as hard spheres colliding elastically with the walls of the container. Is this model realistic?
16. In view of the fact that hot air rises, why does it generally become cooler as you climb a mountain? (Note that air is a poor thermal conductor.)

PROBLEMS

1, 2, 3 = straightforward, intermediate, challenging ☐ = full solution available in the *Student Solutions Manual and Study Guide*

WEB = solution posted at <http://www.saunderscollege.com/physics/>  = Computer useful in solving problem  = Interactive Physics

☐ = paired numerical/symbolic problems

Section 21.1 Molecular Model of an Ideal Gas

1. Use the definition of Avogadro's number to find the mass of a helium atom.
2. A sealed cubical container 20.0 cm on a side contains three times Avogadro's number of molecules at a temperature of 20.0°C . Find the force exerted by the gas on one of the walls of the container.
3. In a 30.0-s interval, 500 hailstones strike a glass window with an area of 0.600 m^2 at an angle of 45.0° to the window surface. Each hailstone has a mass of 5.00 g and a speed of 8.00 m/s. If the collisions are elastic, what are the average force and pressure on the window?
4. In a time t , N hailstones strike a glass window of area A at an angle θ to the window surface. Each hailstone has a mass m and a speed v . If the collisions are elastic, what are the average force and pressure on the window?
5. In a period of 1.00 s, 5.00×10^{23} nitrogen molecules strike a wall with an area of 8.00 cm^2 . If the molecules move with a speed of 300 m/s and strike the wall head-on in perfectly elastic collisions, what is the pressure exerted on the wall? (The mass of one N_2 molecule is $4.68 \times 10^{-26}\text{ kg}$.)
6. A 5.00-L vessel contains 2 mol of oxygen gas at a pressure of 8.00 atm. Find the average translational kinetic energy of an oxygen molecule under these conditions.
7. A spherical balloon with a volume of $4\,000\text{ cm}^3$ contains helium at an (inside) pressure of $1.20 \times 10^5\text{ Pa}$. How many moles of helium are in the balloon if each helium atom has an average kinetic energy of $3.60 \times 10^{-22}\text{ J}$?
8. The rms speed of a helium atom at a certain temperature is 1 350 m/s. Find by proportion the rms speed of an oxygen molecule at this temperature. (The molar mass of O_2 is 32.0 g/mol, and the molar mass of He is 4.00 g/mol.)
9. (a) How many atoms of helium gas fill a balloon of diameter 30.0 cm at 20.0°C and 1.00 atm? (b) What is the average kinetic energy of the helium atoms? (c) What is the root-mean-square speed of each helium atom?

10. A 5.00-liter vessel contains nitrogen gas at 27.0°C and 3.00 atm. Find (a) the total translational kinetic energy of the gas molecules and (b) the average kinetic energy per molecule.
- WEB 11. A cylinder contains a mixture of helium and argon gas in equilibrium at 150°C . (a) What is the average kinetic energy for each type of gas molecule? (b) What is the root-mean-square speed for each type of molecule?
12. (a) Show that $1\text{ Pa} = 1\text{ J/m}^3$. (b) Show that the density in space of the translational kinetic energy of an ideal gas is $3P/2$.

Section 21.2 Molar Specific Heat of an Ideal Gas

Note: You may use the data given in Table 21.2.

13. Calculate the change in internal energy of 3.00 mol of helium gas when its temperature is increased by 2.00 K.
14. One mole of air ($C_V = 5R/2$) at 300 K and confined in a cylinder under a heavy piston occupies a volume of 5.00 L. Determine the new volume of the gas if 4.40 kJ of energy is transferred to the air by heat.
- WEB 15. One mole of hydrogen gas is heated at constant pressure from 300 K to 420 K. Calculate (a) the energy transferred by heat to the gas, (b) the increase in its internal energy, and (c) the work done by the gas.
16. In a constant-volume process, 209 J of energy is transferred by heat to 1.00 mol of an ideal monatomic gas initially at 300 K. Find (a) the increase in internal energy of the gas, (b) the work it does, and (c) its final temperature.
17. A house has well-insulated walls. It contains a volume of 100 m^3 of air at 300 K. (a) Calculate the energy required to increase the temperature of this air by 1.00°C . (b) If this energy could be used to lift an object of mass m through a height of 2.00 m, what is the value of m ?
18. A vertical cylinder with a heavy piston contains air at 300 K. The initial pressure is 200 kPa, and the initial volume is 0.350 m^3 . Take the molar mass of air as 28.9 g/mol and assume that $C_V = 5R/2$. (a) Find the specific heat of air at constant volume in units of $\text{J/kg}\cdot^\circ\text{C}$. (b) Calculate the mass of the air in the cylinder. (c) Suppose the piston is held fixed. Find the energy input required to raise the temperature of the air to 700 K. (d) Assume again the conditions of the initial state and that the heavy piston is free to move. Find the energy input required to raise the temperature to 700 K.
19. A 1-L Thermos bottle is full of tea at 90°C . You pour out one cup and immediately screw the stopper back on. Make an order-of-magnitude estimate of the change in temperature of the tea remaining in the flask that results from the admission of air at room temperature. State the quantities you take as data and the values you measure or estimate for them.
20. For a diatomic ideal gas, $C_V = 5R/2$. One mole of this gas has pressure P and volume V . When the gas is heated, its pressure triples and its volume doubles. If this heating process includes two steps, the first at con-

stant pressure and the second at constant volume, determine the amount of energy transferred to the gas by heat.

21. One mole of an ideal monatomic gas is at an initial temperature of 300 K. The gas undergoes an isovolumetric process, acquiring 500 J of energy by heat. It then undergoes an isobaric process, losing this same amount of energy by heat. Determine (a) the new temperature of the gas and (b) the work done on the gas.
22. A container has a mixture of two gases: n_1 moles of gas 1, which has a molar specific heat C_1 ; and n_2 moles of gas 2, which has a molar specific heat C_2 . (a) Find the molar specific heat of the mixture. (b) What is the molar specific heat if the mixture has m gases in the amounts $n_1, n_2, n_3, \dots, n_m$, and molar specific heats $C_1, C_2, C_3, \dots, C_m$, respectively?
23. One mole of an ideal diatomic gas with $C_V = 5R/2$ occupies a volume V_i at a pressure P_i . The gas undergoes a process in which the pressure is proportional to the volume. At the end of the process, it is found that the rms speed of the gas molecules has doubled from its initial value. Determine the amount of energy transferred to the gas by heat.

Section 21.3 Adiabatic Processes for an Ideal Gas

24. During the compression stroke of a certain gasoline engine, the pressure increases from 1.00 atm to 20.0 atm. Assuming that the process is adiabatic and that the gas is ideal, with $\gamma = 1.40$, (a) by what factor does the volume change and (b) by what factor does the temperature change? (c) If the compression starts with 0.016 0 mol of gas at 27.0°C , find the values of Q , W , and ΔE_{int} that characterize the process.
25. Two moles of an ideal gas ($\gamma = 1.40$) expands slowly and adiabatically from a pressure of 5.00 atm and a volume of 12.0 L to a final volume of 30.0 L. (a) What is the final pressure of the gas? (b) What are the initial and final temperatures? (c) Find Q , W , and ΔE_{int} .
26. Air ($\gamma = 1.40$) at 27.0°C and at atmospheric pressure is drawn into a bicycle pump that has a cylinder with an inner diameter of 2.50 cm and a length of 50.0 cm. The down stroke adiabatically compresses the air, which reaches a gauge pressure of 800 kPa before entering the tire. Determine (a) the volume of the compressed air and (b) the temperature of the compressed air. (c) The pump is made of steel and has an inner wall that is 2.00 mm thick. Assume that 4.00 cm of the cylinder's length is allowed to come to thermal equilibrium with the air. What will be the increase in wall temperature?
27. Air in a thundercloud expands as it rises. If its initial temperature was 300 K, and if no energy is lost by thermal conduction on expansion, what is its temperature when the initial volume has doubled?
28. How much work is required to compress 5.00 mol of air at 20.0°C and 1.00 atm to one tenth of the original vol-

ume by (a) an isothermal process and (b) an adiabatic process? (c) What is the final pressure in each of these two cases?

29. Four liters of a diatomic ideal gas ($\gamma = 1.40$) confined to a cylinder is subject to a closed cycle. Initially, the gas is at 1.00 atm and at 300 K. First, its pressure is tripled under constant volume. Then, it expands adiabatically to its original pressure. Finally, the gas is compressed isobarically to its original volume. (a) Draw a PV diagram of this cycle. (b) Determine the volume of the gas at the end of the adiabatic expansion. (c) Find the temperature of the gas at the start of the adiabatic expansion. (d) Find the temperature at the end of the cycle. (e) What was the net work done for this cycle?
30. A diatomic ideal gas ($\gamma = 1.40$) confined to a cylinder is subjected to a closed cycle. Initially, the gas is at P_i , V_i , and T_i . First, its pressure is tripled under constant volume. Then, it expands adiabatically to its original pressure. Finally, the gas is compressed isobarically to its original volume. (a) Draw a PV diagram of this cycle. (b) Determine the volume of the gas at the end of the adiabatic expansion. (c) Find the temperature of the gas at the start of the adiabatic expansion. (d) Find the temperature at the end of the cycle. (e) What was the net work done for this cycle?
31. During the power stroke in a four-stroke automobile engine, the piston is forced down as the mixture of gas and air undergoes an adiabatic expansion. Assume that (1) the engine is running at 2 500 rpm, (2) the gauge pressure right before the expansion is 20.0 atm, (3) the volumes of the mixture right before and after the expansion are 50.0 and 400 cm³, respectively (Fig.

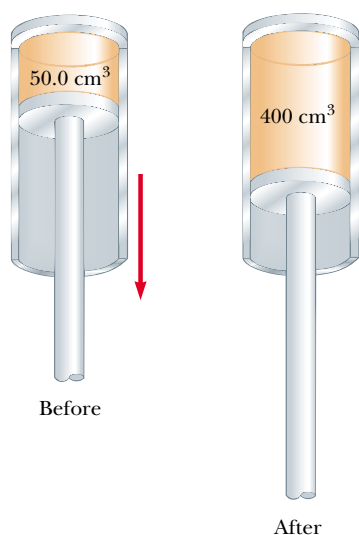


Figure P21.31

P21.31), (4) the time involved in the expansion is one-fourth that of the total cycle, and (5) the mixture behaves like an ideal gas, with $\gamma = 1.40$. Find the average power generated during the expansion.

Section 21.4 The Equipartition of Energy

32. A certain molecule has f degrees of freedom. Show that a gas consisting of such molecules has the following properties: (1) its total internal energy is $f n R T / 2$; (2) its molar specific heat at constant volume is $f R / 2$; (3) its molar specific heat at constant pressure is $(f + 2) R / 2$; (4) the ratio $\gamma = C_p / C_v = (f + 2) / f$.
- WEB 33. Consider 2.00 mol of an ideal diatomic gas. Find the total heat capacity at constant volume and at constant pressure (a) if the molecules rotate but do not vibrate and (b) if the molecules both rotate and vibrate.
34. Inspecting the magnitudes of C_v and C_p for the diatomic and polyatomic gases in Table 21.2, we find that the values increase with increasing molecular mass. Give a qualitative explanation of this observation.
35. In a crude model (Fig. P21.35) of a rotating diatomic molecule of chlorine (Cl_2), the two Cl atoms are 2.00×10^{-10} m apart and rotate about their center of mass with angular speed $\omega = 2.00 \times 10^{12}$ rad/s. What is the rotational kinetic energy of one molecule of Cl_2 , which has a molar mass of 70.0 g/mol?

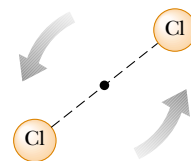


Figure P21.35

Section 21.5 The Boltzmann Distribution Law

Section 21.6 Distribution of Molecular Speeds

36. One cubic meter of atomic hydrogen at 0°C contains approximately 2.70×10^{25} atoms at atmospheric pressure. The first excited state of the hydrogen atom has an energy of 10.2 eV above the lowest energy level, which is called the *ground state*. Use the Boltzmann factor to find the number of atoms in the first excited state at 0°C and at 10 000°C.
37. If convection currents (weather) did not keep the Earth's lower atmosphere stirred up, its chemical composition would change somewhat with altitude because the various molecules have different masses. Use the law of atmospheres to determine how the equilibrium ratio of oxygen to nitrogen molecules changes between sea level and 10.0 km. Assume a uniform temperature of 300 K and take the masses to be 32.0 u for oxygen (O_2) and 28.0 u for nitrogen (N_2).

38. A mixture of two gases diffuses through a filter at rates proportional to the gases' rms speeds. (a) Find the ratio of speeds for the two isotopes of chlorine, ^{35}Cl and ^{37}Cl , as they diffuse through the air. (b) Which isotope moves faster?
39. Fifteen identical particles have various speeds: one has a speed of 2.00 m/s; two have a speed of 3.00 m/s; three have a speed of 5.00 m/s; four have a speed of 7.00 m/s; three have a speed of 9.00 m/s; and two have a speed of 12.0 m/s. Find (a) the average speed, (b) the rms speed, and (c) the most probable speed of these particles.
40. Gaseous helium is in thermal equilibrium with liquid helium at 4.20 K. Even though it is on the point of condensation, model the gas as ideal and determine the most probable speed of a helium atom (mass = 6.64×10^{-27} kg) in it.
41. From the Maxwell-Boltzmann speed distribution, show that the most probable speed of a gas molecule is given by Equation 21.29. Note that the most probable speed corresponds to the point at which the slope of the speed distribution curve, dN_v/dv , is zero.
42. **Review Problem.** At what temperature would the average speed of helium atoms equal (a) the escape speed from Earth, 1.12×10^4 m/s, and (b) the escape speed from the Moon, 2.37×10^3 m/s? (See Chapter 14 for a discussion of escape speed, and note that the mass of a helium atom is 6.64×10^{-27} kg.)
43. A gas is at 0°C . If we wish to double the rms speed of the gas's molecules, by how much must we raise its temperature?
44. The latent heat of vaporization for water at room temperature is 2430 J/g. (a) How much kinetic energy does each water molecule that evaporates possess before it evaporates? (b) Find the pre-evaporation rms speed of a water molecule that is evaporating. (c) What is the effective temperature of these molecules (modeled as if they were already in a thin gas)? Why do these molecules not burn you?

(Optional)

Section 21.7 Mean Free Path

45. In an ultrahigh vacuum system, the pressure is measured to be 1.00×10^{-10} torr (where 1 torr = 133 Pa). Assume that the gas molecules have a molecular diameter of 3.00×10^{-10} m and that the temperature is 300 K. Find (a) the number of molecules in a volume of 1.00 m^3 , (b) the mean free path of the molecules, and (c) the collision frequency, assuming an average speed of 500 m/s.
46. In deep space it is reported that there is only one particle per cubic meter. Using the average temperature of 3.00 K and assuming that the particle is H_2 (with a diameter of 0.200 nm), (a) determine the mean free path of the particle and the average time between collisions. (b) Repeat part (a), assuming that there is only one particle per cubic centimeter.
47. Show that the mean free path for the molecules of an ideal gas at temperature T and pressure P is
- $$\ell = \frac{k_B T}{\sqrt{2} \pi d^2 P}$$
- where d is the molecular diameter.
48. In a tank full of oxygen, how many molecular diameters d (on average) does an oxygen molecule travel (at 1.00 atm and 20.0°C) before colliding with another O_2 molecule? (The diameter of the O_2 molecule is approximately 3.60×10^{-10} m.)
49. Argon gas at atmospheric pressure and 20.0°C is confined in a 1.00-m^3 vessel. The effective hard-sphere diameter of the argon atom is 3.10×10^{-10} m. (a) Determine the mean free path ℓ . (b) Find the pressure when the mean free path is $\ell = 1.00$ m. (c) Find the pressure when $\ell = 3.10 \times 10^{-10}$ m.

ADDITIONAL PROBLEMS

50. The dimensions of a room are $4.20 \text{ m} \times 3.00 \text{ m} \times 2.50 \text{ m}$. (a) Find the number of molecules of air in it at atmospheric pressure and 20.0°C . (b) Find the mass of this air, assuming that the air consists of diatomic molecules with a molar mass of 28.9 g/mol. (c) Find the average kinetic energy of a molecule. (d) Find the root-mean-square molecular speed. (e) On the assumption that the specific heat is a constant independent of temperature, we have $E_{\text{int}} = 5nRT/2$. Find the internal energy in the air. (f) Find the internal energy of the air in the room at 25.0°C .
51. The function $E_{\text{int}} = 3.50nRT$ describes the internal energy of a certain ideal gas. A sample comprising 2.00 mol of the gas always starts at pressure 100 kPa and temperature 300 K. For each one of the following processes, determine the final pressure, volume, and temperature; the change in internal energy of the gas; the energy added to the gas by heat; and the work done by the gas: (a) The gas is heated at constant pressure to 400 K. (b) The gas is heated at constant volume to 400 K. (c) The gas is compressed at constant temperature to 120 kPa. (d) The gas is compressed adiabatically to 120 kPa.
52. Twenty particles, each of mass m and confined to a volume V , have various speeds: two have speed v ; three have speed $2v$; five have speed $3v$; four have speed $4v$; three have speed $5v$; two have speed $6v$; one has speed $7v$. Find (a) the average speed, (b) the rms speed, (c) the most probable speed, (d) the pressure that the particles exert on the walls of the vessel, and (e) the average kinetic energy per particle.
- WEB 53. A cylinder contains n mol of an ideal gas that undergoes an adiabatic process. (a) Starting with the expression

$W = \int P dV$ and using the expression $PV^\gamma = \text{constant}$, show that the work done is

$$W = \left(\frac{1}{\gamma - 1} \right) (P_i V_i - P_f V_f)$$

(b) Starting with the first law equation in differential form, prove that the work done also is equal to $nC_V(T_i - T_f)$. Show that this result is consistent with the equation given in part (a).

54. A vessel contains 1.00×10^4 oxygen molecules at 500 K. (a) Make an accurate graph of the Maxwell speed distribution function versus speed with points at speed intervals of 100 m/s. (b) Determine the most probable speed from this graph. (c) Calculate the average and rms speeds for the molecules and label these points on your graph. (d) From the graph, estimate the fraction of molecules having speeds in the range of 300 m/s to 600 m/s.
55. **Review Problem.** Oxygen at pressures much greater than 1 atm is toxic to lung cells. By weight, what ratio of helium gas (He) to oxygen gas (O_2) must be used by a scuba diver who is to descend to an ocean depth of 50.0 m?
56. A cylinder with a piston contains 1.20 kg of air at 25.0°C and 200 kPa. Energy is transferred into the system by heat as it is allowed to expand, with the pressure rising to 400 kPa. Throughout the expansion, the relationship between pressure and volume is given by

$$P = CV^{1/2}$$

where C is a constant. (a) Find the initial volume. (b) Find the final volume. (c) Find the final temperature. (d) Find the work that the air does. (e) Find the energy transferred by heat. Take $M = 28.9$ g/mol.

- WEB 57. The compressibility κ of a substance is defined as the fractional change in volume of that substance for a given change in pressure:

$$\kappa = -\frac{1}{V} \frac{dV}{dP}$$

(a) Explain why the negative sign in this expression ensures that κ is always positive. (b) Show that if an ideal gas is compressed isothermally, its compressibility is given by $\kappa_1 = 1/P$. (c) Show that if an ideal gas is compressed adiabatically, its compressibility is given by $\kappa_2 = 1/\gamma P$. (d) Determine values for κ_1 and κ_2 for a monatomic ideal gas at a pressure of 2.00 atm.

58. **Review Problem.** (a) Show that the speed of sound in an ideal gas is

$$v = \sqrt{\frac{\gamma RT}{M}}$$

where M is the molar mass. Use the general expression for the speed of sound in a fluid from Section 17.1; the definition of the bulk modulus from Section 12.4; and the result of Problem 57 in this chapter. As a sound

wave passes through a gas, the compressions are either so rapid or so far apart that energy flow by heat is prevented by lack of time or by effective thickness of insulation. The compressions and rarefactions are adiabatic. (b) Compute the theoretical speed of sound in air at 20°C and compare it with the value given in Table 17.1. Take $M = 28.9$ g/mol. (c) Show that the speed of sound in an ideal gas is

$$v = \sqrt{\frac{\gamma k_B T}{m}}$$

where m is the mass of one molecule. Compare your result with the most probable, the average, and the rms molecular speeds.

59. For a Maxwellian gas, use a computer or programmable calculator to find the numerical value of the ratio $N_v(v)/N_v(v_{\text{mp}})$ for the following values of v : $v = (v_{\text{mp}}/50), (v_{\text{mp}}/10), (v_{\text{mp}}/2), v_{\text{mp}}, 2v_{\text{mp}}, 10v_{\text{mp}}, 50v_{\text{mp}}$. Give your results to three significant figures.
60. A pitcher throws a 0.142-kg baseball at 47.2 m/s (Fig. P21.60). As it travels 19.4 m, the ball slows to 42.5 m/s because of air resistance. Find the change in temperature of the air through which it passes. To find the greatest possible temperature change, you may make the following assumptions: Air has a molar heat capacity of $C_p = 7R/2$ and an equivalent molar mass of 28.9 g/mol. The process is so rapid that the cover of the baseball acts as thermal insulation, and the temperature of the ball itself does not change. A change in temperature happens initially only for the air in a cylinder 19.4 m in length and 3.70 cm in radius. This air is initially at 20.0°C .



Figure P21.60 Nolan Ryan hurls the baseball for his 5 000th strikeout. (Joe Patronite/ALLSPORT)

61. Consider the particles in a *gas centrifuge*, a device that separates particles of different mass by whirling them in a circular path of radius r at angular speed ω . Newton's second law applied to circular motion states that a force of magnitude equal to $m\omega^2 r$ acts on a particle. (a) Discuss how a gas centrifuge can be used to separate particles of different mass. (b) Show that the density of the particles as a function of r is

$$n(r) = n_0 e^{m\omega^2 r^2 / 2k_B T}$$

62. Verify Equations 21.27 and 21.28 for the rms and average speeds of the molecules of a gas at a temperature T . Note that the average value of v^n is

$$\overline{v^n} = \frac{1}{N} \int_0^\infty v^n N_v dv$$

and make use of the definite integrals

$$\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2} \quad \int_0^\infty x^4 e^{-ax^2} dx = \frac{3}{8a^2} \sqrt{\frac{\pi}{a}}$$

63. A sample of a monatomic ideal gas occupies 5.00 L at atmospheric pressure and 300 K (point A in Figure P21.63). It is heated at constant volume to 3.00 atm (point B). Then, it is allowed to expand isothermally to 1.00 atm (point C) and at last is compressed isobarically to its original state. (a) Find the number of moles in the sample. (b) Find the temperatures at points B and C and the volume at point C. (c) Assuming that the specific heat does not depend on temperature, so that $E_{\text{int}} = 3nRT/2$, find the internal energy at points A, B,

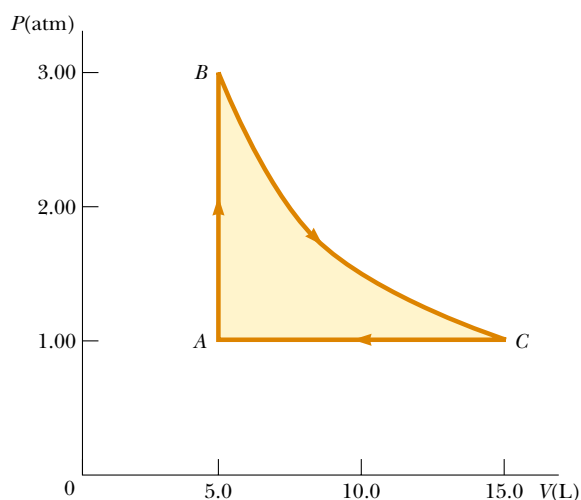


Figure P21.63

and C. (d) Tabulate P , V , T , and E_{int} at the states at points A, B, and C. (e) Now consider the processes $A \rightarrow B$, $B \rightarrow C$, and $C \rightarrow A$. Describe just how to carry out each process experimentally. (f) Find Q , W , and ΔE_{int} for each of the processes. (g) For the whole cycle $A \rightarrow B \rightarrow C \rightarrow A$, find Q , W , and ΔE_{int} .

64. If you can't walk to outer space, can you walk at least half way? (a) Show that the fraction of particles below an altitude h in the atmosphere is

$$f = 1 - e^{(-mgh/k_B T)}$$

(b) Use this result to show that half the particles are below the altitude $h' = k_B T \ln(2)/mg$. What is the value of h' for the Earth? (Assume a temperature of 270 K, and note that the average molar mass for air is 28.9 g/mol.)

65. This problem will help you to think about the size of molecules. In the city of Beijing, a restaurant keeps a pot of chicken broth simmering continuously. Every morning it is topped off to contain 10.0 L of water, along with a fresh chicken, vegetables, and spices. The soup is thoroughly stirred. The molar mass of water is 18.0 g/mol. (a) Find the number of molecules of water in the pot. (b) During a certain month, 90.0% of the broth was served each day to people who then emigrated immediately. Of the water molecules present in the pot on the first day of the month, when was the last one likely to have been ladled out of the pot? (c) The broth has been simmering for centuries, through wars, earthquakes, and stove repairs. Suppose that the water that was in the pot long ago has thoroughly mixed into the Earth's hydrosphere, of mass 1.32×10^{21} kg. How many of the water molecules originally in the pot are likely to be present in it again today?
66. **Review Problem.** (a) If it has enough kinetic energy, a molecule at the surface of the Earth can escape the Earth's gravitation. Using the principle of conservation of energy, show that the minimum kinetic energy needed for escape is mgR , where m is the mass of the molecule, g is the free-fall acceleration at the surface of the Earth, and R is the radius of the Earth. (b) Calculate the temperature for which the minimum escape kinetic energy is ten times the average kinetic energy of an oxygen molecule.

67. Using multiple laser beams, physicists have been able to cool and trap sodium atoms in a small region. In one experiment, the temperature of the atoms was reduced to 0.240 mK. (a) Determine the rms speed of the sodium atoms at this temperature. The atoms can be trapped for about 1.00 s. The trap has a linear dimension of roughly 1.00 cm. (b) Approximately how long would it take an atom to wander out of the trap region if there were no trapping action?

ANSWERS TO QUICK QUIZZES

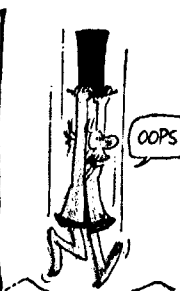
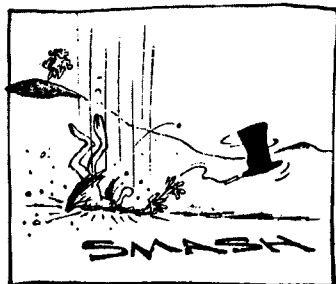
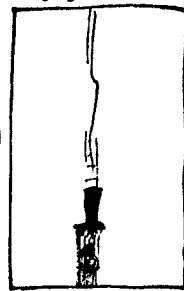
- 21.1** Although a molecule moves very rapidly, it does not travel far before it collides with another molecule. The collision deflects the molecule from its original path. Eventually, a perfume molecule will make its way from one end of the room to the other, but the path it takes is much longer than the straight-line distance from the perfume bottle to your nose.
- 21.2** (c) E_{int} stays the same. According to Equation 21.10, E_{int} is a function of temperature only. Along an isotherm, T

is constant by definition. Therefore, the internal energy of the gas does not change.

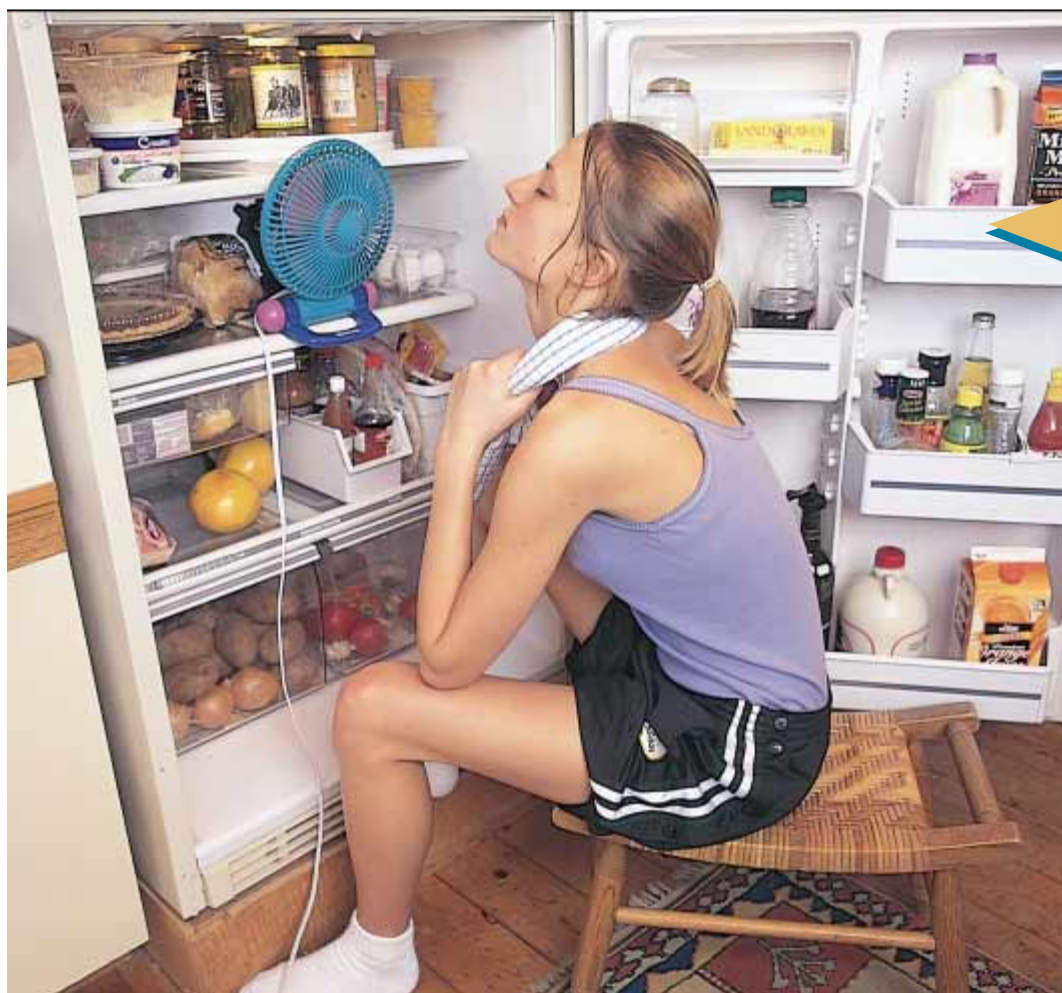
- 21.3** The area under each curve represents the number of molecules in that particular velocity range. The $T = 900 \text{ K}$ curve has many more molecules moving between 800 m/s and 1000 m/s than does the $T = 300 \text{ K}$ curve.

B.C.

79

**By John Hart****SMASH****I MADE IT.**

By permission of John Hart and Field Enterprises, Inc.



PUZZLER

The purpose of a refrigerator is to keep its contents cool. Beyond the attendant increase in your electricity bill, there is another good reason you should not try to cool the kitchen on a hot day by leaving the refrigerator door open. What might this reason be?

(Charles D. Winters)

Heat Engines, Entropy, and the Second Law of Thermodynamics

chapter

22

Chapter Outline

- 22.1** Heat Engines and the Second Law of Thermodynamics
- 22.2** Reversible and Irreversible Processes
- 22.3** The Carnot Engine
- 22.4** Gasoline and Diesel Engines

- 22.5** Heat Pumps and Refrigerators
- 22.6** Entropy
- 22.7** Entropy Changes in Irreversible Processes
- 22.8** (Optional) Entropy on a Microscopic Scale

The first law of thermodynamics, which we studied in Chapter 20, is a statement of conservation of energy, generalized to include internal energy. This law states that a change in internal energy in a system can occur as a result of energy transfer by heat or by work, or by both. As was stated in Chapter 20, the law makes no distinction between the results of heat and the results of work—either heat or work can cause a change in internal energy. However, an important distinction between the two is not evident from the first law. One manifestation of this distinction is that it is impossible to convert internal energy completely to mechanical energy by taking a substance through a thermodynamic cycle such as in a *heat engine*, a device we study in this chapter.

Although the first law of thermodynamics is very important, it makes no distinction between processes that occur spontaneously and those that do not. However, we find that only certain types of energy-conversion and energy-transfer processes actually take place. The *second law of thermodynamics*, which we study in this chapter, establishes which processes do and which do not occur in nature. The following are examples of processes that proceed in only one direction, governed by the second law:

- When two objects at different temperatures are placed in thermal contact with each other, energy always flows by heat from the warmer to the cooler, never from the cooler to the warmer.
- A rubber ball dropped to the ground bounces several times and eventually comes to rest, but a ball lying on the ground never begins bouncing on its own.
- An oscillating pendulum eventually comes to rest because of collisions with air molecules and friction at the point of suspension. The mechanical energy of the system is converted to internal energy in the air, the pendulum, and the suspension; the reverse conversion of energy never occurs.

All these processes are *irreversible*—that is, they are processes that occur naturally in one direction only. No irreversible process has ever been observed to run backward—if it were to do so, it would violate the second law of thermodynamics.¹

From an engineering standpoint, perhaps the most important implication of the second law is the limited efficiency of heat engines. The second law states that a machine capable of continuously converting internal energy completely to other forms of energy in a cyclic process cannot be constructed.

22.1 HEAT ENGINES AND THE SECOND LAW OF THERMODYNAMICS



10.8 A heat engine is a device that converts internal energy to mechanical energy. For instance, in a typical process by which a power plant produces electricity, coal or some other fuel is burned, and the high-temperature gases produced are used to convert liquid water to steam. This steam is directed at the blades of a turbine, setting it into rotation. The mechanical energy associated with this rotation is used to drive an electric generator. Another heat engine—the internal combustion engine in an automobile—uses energy from a burning fuel to perform work that results in the motion of the automobile.

¹ Although we have never *observed* a process occurring in the time-reversed sense, it is *possible* for it to occur. As we shall see later in the chapter, however, such a process is highly improbable. From this viewpoint, we say that processes occur with a vastly greater probability in one direction than in the opposite direction.



Figure 22.1 This steam-driven locomotive runs from Durango to Silverton, Colorado. It obtains its energy by burning wood or coal. The generated energy vaporizes water into steam, which powers the locomotive. (This locomotive must take on water from tanks located along the route to replace steam lost through the funnel.) Modern locomotives use diesel fuel instead of wood or coal. Whether old-fashioned or modern, such locomotives are heat engines, which extract energy from a burning fuel and convert a fraction of it to mechanical energy.

A heat engine carries some working substance through a cyclic process during which (1) the working substance absorbs energy from a high-temperature energy reservoir, (2) work is done by the engine, and (3) energy is expelled by the engine to a lower-temperature reservoir. As an example, consider the operation of a steam engine (Fig. 22.1), in which the working substance is water. The water in a boiler absorbs energy from burning fuel and evaporates to steam, which then does work by expanding against a piston. After the steam cools and condenses, the liquid water produced returns to the boiler and the cycle repeats.

It is useful to represent a heat engine schematically as in Figure 22.2. The engine absorbs a quantity of energy Q_h from the hot reservoir, does work W , and then gives up a quantity of energy Q_c to the cold reservoir. Because the working substance goes through a cycle, its initial and final internal energies are equal, and so $\Delta E_{\text{int}} = 0$. Hence, from the first law of thermodynamics, $\Delta E_{\text{int}} = Q - W$, and with no change in internal energy, **the net work W done by a heat engine is equal to the net energy Q_{net} flowing through it.** As we can see from Figure 22.2, $Q_{\text{net}} = Q_h - Q_c$; therefore,

$$W = Q_h - Q_c \quad (22.1)$$

In this expression and in many others throughout this chapter, to be consistent with traditional treatments of heat engines, we take both Q_h and Q_c to be positive quantities, even though Q_c represents energy leaving the engine. In discussions of heat engines, we shall describe energy leaving a system with an explicit minus sign,



Lord Kelvin British physicist and mathematician (1824–1907) Born William Thomson in Belfast, Kelvin was the first to propose the use of an absolute scale of temperature. The Kelvin temperature scale is named in his honor. Kelvin's work in thermodynamics led to the idea that energy cannot pass spontaneously from a colder body to a hotter body. (J. L. Charmet/SPL/Photo Researchers, Inc.)

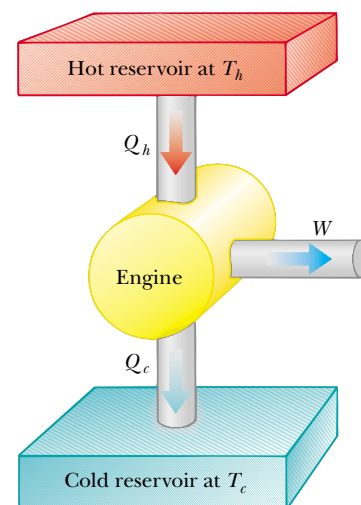


Figure 22.2 Schematic representation of a heat engine. The engine absorbs energy Q_h from the hot reservoir, expels energy Q_c to the cold reservoir, and does work W .

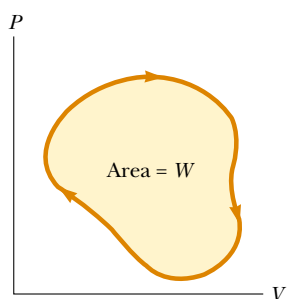


Figure 22.3 *PV* diagram for an arbitrary cyclic process. The value of the net work done equals the area enclosed by the curve.

as in Equation 22.1. Also note that we model the energy input and output for the heat engine as heat, as it often is; however, the energy transfer could occur by another mechanism.

The net work done in a cyclic process is the area enclosed by the curve representing the process on a *PV* diagram. This is shown for an arbitrary cyclic process in Figure 22.3.

The **thermal efficiency** e of a heat engine is defined as the ratio of the net work done by the engine during one cycle to the energy absorbed at the higher temperature during the cycle:

$$e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} \quad (22.2)$$

We can think of the efficiency as the ratio of what you get (mechanical work) to what you give (energy transfer at the higher temperature). In practice, we find that all heat engines expel only a fraction of the absorbed energy as mechanical work and that consequently the efficiency is less than 100%. For example, a good automobile engine has an efficiency of about 20%, and diesel engines have efficiencies ranging from 35% to 40%.

Equation 22.2 shows that a heat engine has 100% efficiency ($e = 1$) only if $Q_c = 0$ —that is, if no energy is expelled to the cold reservoir. In other words, a heat engine with perfect efficiency would have to expel all of the absorbed energy as mechanical work. On the basis of the fact that efficiencies of real engines are well below 100%, the **Kelvin–Planck** form of the **second law of thermodynamics** states the following:

Kelvin–Planck statement of the second law of thermodynamics

It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the absorption of energy from a reservoir and the performance of an equal amount of work.

This statement of the second law means that, during the operation of a heat engine, W can never be equal to Q_h , or, alternatively, that some energy Q_c must be

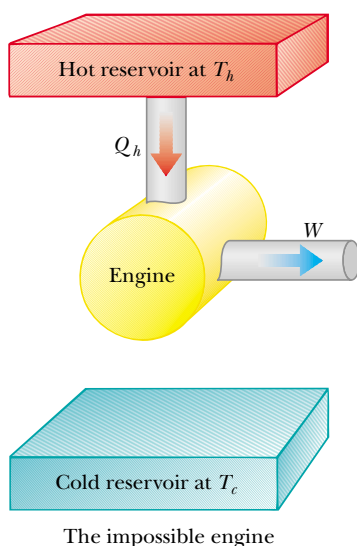


Figure 22.4 Schematic diagram of a heat engine that absorbs energy Q_h from a hot reservoir and does an equivalent amount of work. It is impossible to construct such a perfect engine.

rejected to the environment. Figure 22.4 is a schematic diagram of the impossible “perfect” heat engine.

The first and second laws of thermodynamics can be summarized as follows: The first law specifies that **we cannot get more energy out of a cyclic process by work than the amount of energy we put in**, and the second law states that **we cannot break even because we must put more energy in, at the higher temperature, than the net amount of energy we get out by work**.

EXAMPLE 22.1 The Efficiency of an Engine

Find the efficiency of a heat engine that absorbs 2 000 J of energy from a hot reservoir and exhausts 1 500 J to a cold reservoir.

Equation 22.2:

$$e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{1\,500\text{ J}}{2\,000\text{ J}} = 0.25, \text{ or } 25\%$$

Solution To calculate the efficiency of the engine, we use

Refrigerators and Heat Pumps

Refrigerators and **heat pumps** are heat engines running in reverse. Here, we introduce them briefly for the purposes of developing an alternate statement of the second law; we shall discuss them more fully in Section 22.5.

In a refrigerator or heat pump, the engine absorbs energy Q_c from a cold reservoir and expels energy Q_h to a hot reservoir (Fig. 22.5). This can be accomplished only if work is done *on* the engine. From the first law, we know that the energy given up to the hot reservoir must equal the sum of the work done and the energy absorbed from the cold reservoir. Therefore, the refrigerator or heat pump transfers energy from a colder body (for example, the contents of a kitchen refrigerator or the winter air outside a building) to a hotter body (the air in the kitchen or a room in the building). In practice, it is desirable to carry out this process with a minimum of work. If it could be accomplished without doing any work, then the refrigerator or heat pump would be “perfect” (Fig. 22.6). Again, the existence of

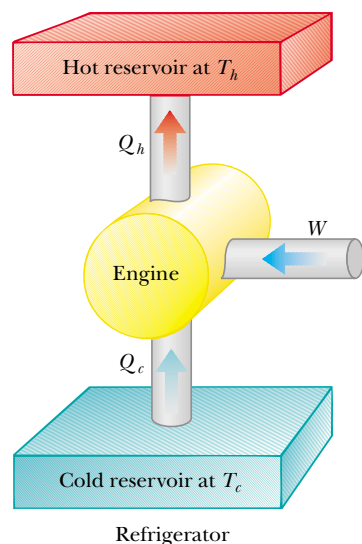


Figure 22.5 Schematic diagram of a refrigerator, which absorbs energy Q_c from a cold reservoir and expels energy Q_h to a hot reservoir. Work W is done *on* the refrigerator. A heat pump, which can be used to heat or cool a building, works the same way.

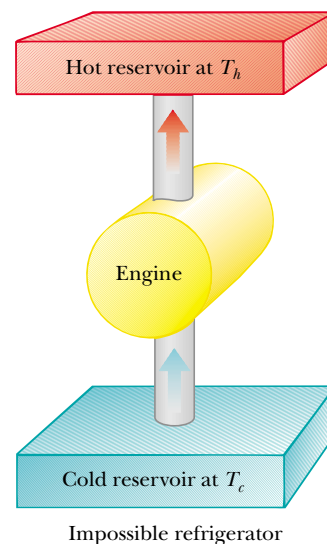


Figure 22.6 Schematic diagram of an impossible refrigerator or heat pump—that is, one that absorbs energy Q_c from a cold reservoir and expels an equivalent amount of energy to a hot reservoir with $W = 0$.

Clausius statement of the second law of thermodynamics

such a device would be in violation of the second law of thermodynamics, which in the form of the **Clausius statement**² states:

It is impossible to construct a cyclical machine whose sole effect is the continuous transfer of energy from one object to another object at a higher temperature without the input of energy by work.

In simpler terms, **energy does not flow spontaneously from a cold object to a hot object.** For example, we cool homes in summer using heat pumps called *air conditioners*. The air conditioner pumps energy from the cool room in the home to the warm air outside. This direction of energy transfer requires an input of energy to the air conditioner, which is supplied by the electric power company.

The Clausius and Kelvin–Planck statements of the second law of thermodynamics appear, at first sight, to be unrelated, but in fact they are equivalent in all respects. Although we do not prove so here, if either statement is false, then so is the other.³

22.2 REVERSIBLE AND IRREVERSIBLE PROCESSES

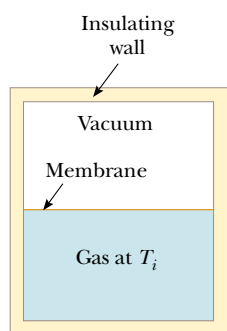


Figure 22.7 Adiabatic free expansion of a gas.

In the next section we discuss a theoretical heat engine that is the most efficient possible. To understand its nature, we must first examine the meaning of reversible and irreversible processes. In a **reversible** process, the system undergoing the process can be returned to its initial conditions along the same path shown on a PV diagram, and every point along this path is an equilibrium state. A process that does not satisfy these requirements is **irreversible**.

All natural processes are known to be irreversible. From the endless number of examples that could be selected, let us examine the adiabatic free expansion of a gas, which was already discussed in Section 20.6, and show that it cannot be reversible. The system that we consider is a gas in a thermally insulated container, as shown in Figure 22.7. A membrane separates the gas from a vacuum. When the membrane is punctured, the gas expands freely into the vacuum. As a result of the puncture, the system has changed because it occupies a greater volume after the expansion. Because the gas does not exert a force through a distance on the surroundings, it does no work on the surroundings as it expands. In addition, no energy is transferred to or from the gas by heat because the container is insulated from its surroundings. Thus, in this adiabatic process, the system has changed but the surroundings have not.

For this process to be reversible, we need to be able to return the gas to its original volume and temperature without changing the surroundings. Imagine that we try to reverse the process by compressing the gas to its original volume. To do so, we fit the container with a piston and use an engine to force the piston inward. During this process, the surroundings change because work is being done by an outside agent on the system. In addition, the system changes because the compression increases the temperature of the gas. We can lower the temperature of the gas by allowing it to come into contact with an external energy reservoir. Although this step returns the gas to its original conditions, the surroundings are

² First expressed by Rudolf Clausius (1822–1888).

³ See, for example, R. P. Bauman, *Modern Thermodynamics and Statistical Mechanics*, New York, Macmillan Publishing Co., 1992.

again affected because energy is being added to the surroundings from the gas. If this energy could somehow be used to drive the engine that we have used to compress the gas, then the net energy transfer to the surroundings would be zero. In this way, the system and its surroundings could be returned to their initial conditions, and we could identify the process as reversible. However, the Kelvin–Planck statement of the second law specifies that the energy removed from the gas to return the temperature to its original value cannot be completely converted to mechanical energy in the form of the work done by the engine in compressing the gas. Thus, we must conclude that the process is irreversible.

We could also argue that the adiabatic free expansion is irreversible by relying on the portion of the definition of a reversible process that refers to equilibrium states. For example, during the expansion, significant variations in pressure occur throughout the gas. Thus, there is no well-defined value of the pressure for the entire system at any time between the initial and final states. In fact, the process cannot even be represented as a path on a PV diagram. The PV diagram for an adiabatic free expansion would show the initial and final conditions as points, but these points would not be connected by a path. Thus, because the intermediate conditions between the initial and final states are not equilibrium states, the process is irreversible.

Although all real processes are always irreversible, some are almost reversible. If a real process occurs very slowly such that the system is always very nearly in an equilibrium state, then the process can be approximated as reversible. For example, let us imagine that we compress a gas very slowly by dropping some grains of sand onto a frictionless piston, as shown in Figure 22.8. We make the process isothermal by placing the gas in thermal contact with an energy reservoir, and we transfer just enough energy from the gas to the reservoir during the process to keep the temperature constant. The pressure, volume, and temperature of the gas are all well defined during the isothermal compression, so each state during the process is an equilibrium state. Each time we add a grain of sand to the piston, the volume of the gas decreases slightly while the pressure increases slightly. Each grain we add represents a change to a new equilibrium state. We can reverse the process by slowly removing grains from the piston.

A general characteristic of a reversible process is that no dissipative effects (such as turbulence or friction) that convert mechanical energy to internal energy can be present. Such effects can be impossible to eliminate completely. Hence, it is not surprising that real processes in nature are irreversible.

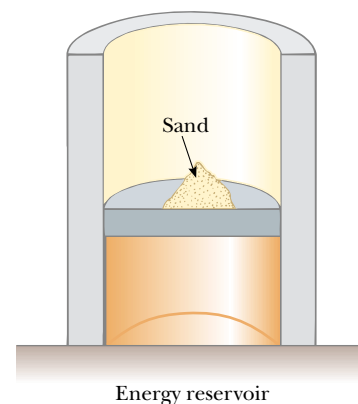


Figure 22.8 A gas in thermal contact with an energy reservoir is compressed slowly as individual grains of sand drop onto the piston. The compression is isothermal and reversible.



Sadi Carnot French physicist (1796–1832) Carnot was the first to show the quantitative relationship between work and heat. In 1824 he published his only work—*Reflections on the Motive Power of Heat*—which reviewed the industrial, political, and economic importance of the steam engine. In it, he defined work as “weight lifted through a height.” (FPG)

22.3 THE CARNOT ENGINE

10.9 In 1824 a French engineer named Sadi Carnot described a theoretical engine, now called a **Carnot engine**, that is of great importance from both practical and theoretical viewpoints. He showed that a heat engine operating in an ideal, reversible cycle—called a **Carnot cycle**—between two energy reservoirs is the most efficient engine possible. Such an ideal engine establishes an upper limit on the efficiencies of all other engines. That is, the net work done by a working substance taken through the Carnot cycle is the greatest amount of work possible for a given amount of energy supplied to the substance at the upper temperature. **Carnot’s theorem** can be stated as follows:

No real heat engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.

To argue the validity of this theorem, let us imagine two heat engines operating between the *same* energy reservoirs. One is a Carnot engine with efficiency e_C , and the other is an engine with efficiency e , which is greater than e_C . We use the more efficient engine to drive the Carnot engine as a Carnot refrigerator. Thus, the output by work of the more efficient engine is matched to the input by work of the

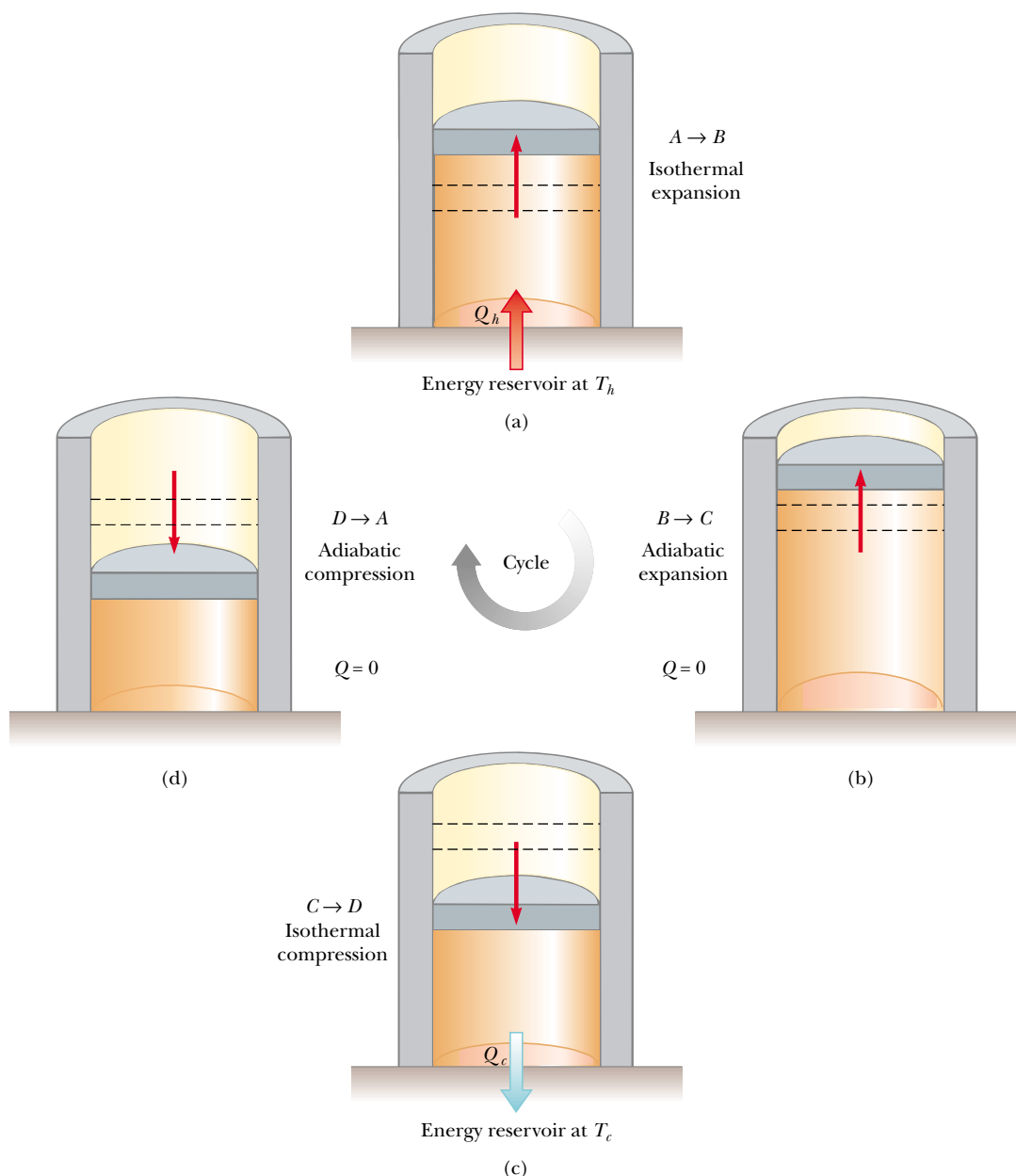


Figure 22.9 The Carnot cycle. In process $A \rightarrow B$, the gas expands isothermally while in contact with a reservoir at T_h . In process $B \rightarrow C$, the gas expands adiabatically ($Q = 0$). In process $C \rightarrow D$, the gas is compressed isothermally while in contact with a reservoir at $T_c < T_h$. In process $D \rightarrow A$, the gas is compressed adiabatically. The upward arrows on the piston indicate that weights are being removed during the expansions, and the downward arrows indicate that weights are being added during the compressions.

Carnot refrigerator. For the *combination* of the engine and refrigerator, then, no exchange by work with the surroundings occurs. Because we have assumed that the engine is more efficient than the refrigerator, the net result of the combination is a transfer of energy from the cold to the hot reservoir without work being done on the combination. According to the Clausius statement of the second law, this is impossible. Hence, the assumption that $e > e_C$ must be false. **All real engines are less efficient than the Carnot engine because they do not operate through a reversible cycle.** The efficiency of a real engine is further reduced by such practical difficulties as friction and energy losses by conduction.

To describe the Carnot cycle taking place between temperatures T_c and T_h , we assume that the working substance is an ideal gas contained in a cylinder fitted with a movable piston at one end. The cylinder's walls and the piston are thermally nonconducting. Four stages of the Carnot cycle are shown in Figure 22.9, and the PV diagram for the cycle is shown in Figure 22.10. The Carnot cycle consists of two adiabatic processes and two isothermal processes, all reversible:

1. Process $A \rightarrow B$ (Fig. 22.9a) is an isothermal expansion at temperature T_h . The gas is placed in thermal contact with an energy reservoir at temperature T_h . During the expansion, the gas absorbs energy Q_h from the reservoir through the base of the cylinder and does work W_{AB} in raising the piston.
2. In process $B \rightarrow C$ (Fig. 22.9b), the base of the cylinder is replaced by a thermally nonconducting wall, and the gas expands adiabatically—that is, no energy enters or leaves the system. During the expansion, the temperature of the gas decreases from T_h to T_c and the gas does work W_{BC} in raising the piston.
3. In process $C \rightarrow D$ (Fig. 22.9c), the gas is placed in thermal contact with an energy reservoir at temperature T_c and is compressed isothermally at temperature T_c . During this time, the gas expels energy Q_c to the reservoir, and the work done by the piston on the gas is W_{CD} .
4. In the final process $D \rightarrow A$ (Fig. 22.9d), the base of the cylinder is replaced by a nonconducting wall, and the gas is compressed adiabatically. The temperature of the gas increases to T_h , and the work done by the piston on the gas is W_{DA} .

The net work done in this reversible, cyclic process is equal to the area enclosed by the path $ABCD$ in Figure 22.10. As we demonstrated in Section 22.1, because the change in internal energy is zero, the net work W done in one cycle equals the net energy transferred into the system, $Q_h - Q_c$. The thermal efficiency of the engine is given by Equation 22.2:

$$e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

In Example 22.2, we show that for a Carnot cycle

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h} \quad (22.3)$$

Hence, the thermal efficiency of a Carnot engine is

$$e_C = 1 - \frac{T_c}{T_h} \quad (22.4)$$

This result indicates that **all Carnot engines operating between the same two temperatures have the same efficiency.**

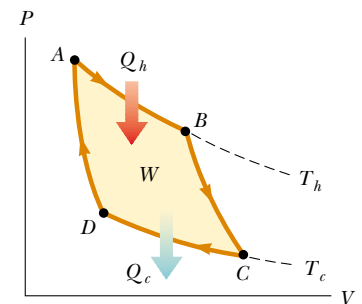


Figure 22.10 PV diagram for the Carnot cycle. The net work done, W , equals the net energy received in one cycle, $Q_h - Q_c$. Note that $\Delta E_{\text{int}} = 0$ for the cycle.

Ratio of energies for a Carnot cycle

Efficiency of a Carnot engine

Equation 22.4 can be applied to any working substance operating in a Carnot cycle between two energy reservoirs. According to this equation, the efficiency is zero if $T_c = T_h$, as one would expect. The efficiency increases as T_c is lowered and as T_h is raised. However, the efficiency can be unity (100%) only if $T_c = 0$ K. Such reservoirs are not available; thus, the maximum efficiency is always less than 100%. In most practical cases, T_c is near room temperature, which is about 300 K. Therefore, one usually strives to increase the efficiency by raising T_h .

EXAMPLE 22.2 Efficiency of the Carnot Engine

Show that the efficiency of a heat engine operating in a Carnot cycle using an ideal gas is given by Equation 22.4.

Solution During the isothermal expansion (process $A \rightarrow B$ in Figure 22.9), the temperature does not change. Thus, the internal energy remains constant. The work done by a gas during an isothermal expansion is given by Equation 20.13. According to the first law, this work is equal to Q_h , the energy absorbed, so that

$$Q_h = W_{AB} = nRT_h \ln \frac{V_B}{V_A}$$

In a similar manner, the energy transferred to the cold reservoir during the isothermal compression $C \rightarrow D$ is

$$Q_c = |W_{CD}| = nRT_c \ln \frac{V_C}{V_D}$$

We take the absolute value of the work because we are defining all values of Q for a heat engine as positive, as mentioned earlier. Dividing the second expression by the first, we find that

$$(1) \quad \frac{Q_c}{Q_h} = \frac{T_c}{T_h} \frac{\ln(V_C/V_D)}{\ln(V_B/V_A)}$$

We now show that the ratio of the logarithmic quantities is unity by establishing a relationship between the ratio of volumes. For any quasi-static, adiabatic process, the pressure and volume are related by Equation 21.18:

$$(2) \quad PV^\gamma = \text{constant}$$

During any reversible, quasi-static process, the ideal gas must also obey the equation of state, $PV = nRT$. Solving this ex-

pression for P and substituting into (2), we obtain

$$\frac{nRT}{V} V^\gamma = \text{constant}$$

which we can write as

$$TV^{\gamma-1} = \text{constant}$$

where we have absorbed nR into the constant right-hand side. Applying this result to the adiabatic processes $B \rightarrow C$ and $D \rightarrow A$, we obtain

$$T_h V_B^{\gamma-1} = T_c V_C^{\gamma-1}$$

$$T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1}$$

Dividing the first equation by the second, we obtain

$$(V_B/V_A)^{\gamma-1} = (V_C/V_D)^{\gamma-1}$$

$$(3) \quad \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Substituting (3) into (1), we find that the logarithmic terms cancel, and we obtain the relationship

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

Using this result and Equation 22.2, we see that the thermal efficiency of the Carnot engine is

$$e_C = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

which is Equation 22.4, the one we set out to prove.

EXAMPLE 22.3 The Steam Engine

A steam engine has a boiler that operates at 500 K. The energy from the burning fuel changes water to steam, and this steam then drives a piston. The cold reservoir's temperature is that of the outside air, approximately 300 K. What is the maximum thermal efficiency of this steam engine?

Solution Using Equation 22.4, we find that the maximum thermal efficiency for any engine operating between these temperatures is

$$e_C = 1 - \frac{T_c}{T_h} = 1 - \frac{300 \text{ K}}{500 \text{ K}} = 0.4, \text{ or } 40\%$$

You should note that this is the highest *theoretical* efficiency of the engine. In practice, the efficiency is considerably lower.

can perform in each cycle if it absorbs 200 J of energy from the hot reservoir during each cycle.

Exercise Determine the maximum work that the engine **Answer** 80 J.

EXAMPLE 22.4 The Carnot Efficiency

The highest theoretical efficiency of a certain engine is 30%. If this engine uses the atmosphere, which has a temperature of 300 K, as its cold reservoir, what is the temperature of its hot reservoir?

Solution We use the Carnot efficiency to find T_h :

$$e_C = 1 - \frac{T_c}{T_h}$$

$$T_h = \frac{T_c}{1 - e_C} = \frac{300 \text{ K}}{1 - 0.30} = 430 \text{ K}$$

22.4 GASOLINE AND DIESEL ENGINES

In a gasoline engine, six processes occur in each cycle; five of these are illustrated in Figure 22.11. In this discussion, we consider the interior of the cylinder above the piston to be the system that is taken through repeated cycles in the operation of the engine. For a given cycle, the piston moves up and down twice. This represents a four-stroke cycle consisting of two upstrokes and two downstrokes. The processes in the cycle can be approximated by the **Otto cycle**, a PV diagram of which is illustrated in Figure 22.12:

1. During the *intake stroke* $O \rightarrow A$ (Fig. 22.11a), the piston moves downward, and a gaseous mixture of air and fuel is drawn into the cylinder at atmospheric pressure. In this process, the volume increases from V_2 to V_1 . This is the energy input part of the cycle, as energy enters the system (the interior of the cylinder) as internal energy stored in the fuel. This is energy transfer by *mass transfer*—that is, the energy is carried with a substance. It is similar to convection, which we studied in Chapter 20.
2. During the *compression stroke* $A \rightarrow B$ (Fig. 22.11b), the piston moves upward, the air–fuel mixture is compressed adiabatically from volume V_1 to volume V_2 , and the temperature increases from T_A to T_B . The work done by the gas is negative, and its value is equal to the area under the curve AB in Figure 22.12.
3. In process $B \rightarrow C$, combustion occurs when the spark plug fires (Fig. 22.11c). This is not one of the strokes of the cycle because it occurs in a very short period of time while the piston is at its highest position. The combustion represents a rapid transformation from internal energy stored in chemical bonds in the fuel to internal energy associated with molecular motion, which is related to temperature. During this time, the pressure and temperature in the cylinder increase rapidly, with the temperature rising from T_B to T_C . The volume, however, remains approximately constant because of the short time interval. As a result, approximately no work is done by the gas. We can model this process in the PV diagram (Fig. 22.12) as that process in which the energy Q_h enters the system. However, in reality this process is a transformation of energy already in the cylinder (from process $O \rightarrow A$) rather than a transfer.
4. In the *power stroke* $C \rightarrow D$ (Fig. 22.11d), the gas expands adiabatically from V_2 to

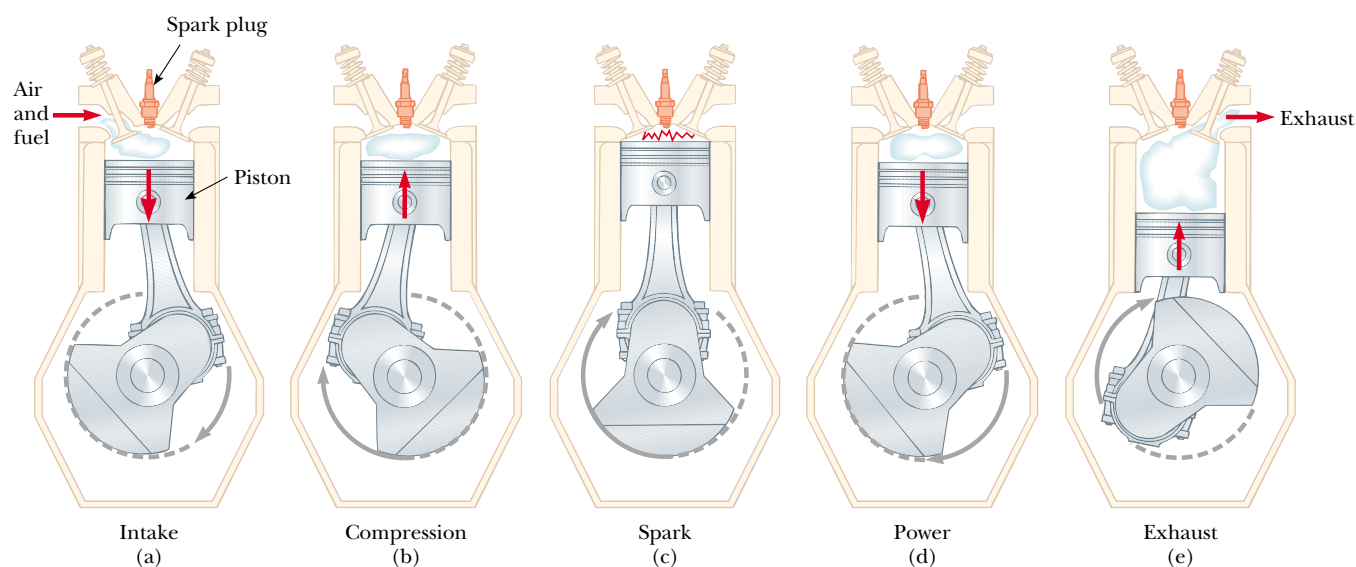


Figure 22.11 The four-stroke cycle of a conventional gasoline engine. (a) In the intake stroke, air is mixed with fuel. (b) The intake valve is then closed, and the air–fuel mixture is compressed by the piston. (c) The mixture is ignited by the spark plug, with the result that the temperature of the mixture increases. (d) In the power stroke, the gas expands against the piston. (e) Finally, the residual gases are expelled, and the cycle repeats.

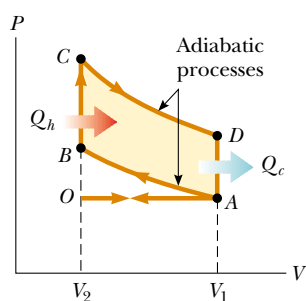


Figure 22.12 PV diagram for the Otto cycle, which approximately represents the processes occurring in an internal combustion engine.

V_1 . This expansion causes the temperature to drop from T_C to T_D . Work is done by the gas in pushing the piston downward, and the value of this work is equal to the area under the curve CD .

5. In the process $D \rightarrow A$ (not shown in Fig. 22.11), an exhaust valve is opened as the piston reaches the bottom of its travel, and the pressure suddenly drops for a short time interval. During this interval, the piston is almost stationary and the volume is approximately constant. Energy is expelled from the interior of the cylinder and continues to be expelled during the next process.
6. In the final process, the *exhaust stroke* $A \rightarrow O$ (Fig. 22.11e), the piston moves upward while the exhaust valve remains open. Residual gases are exhausted at atmospheric pressure, and the volume decreases from V_1 to V_2 . The cycle then repeats.

If the air–fuel mixture is assumed to be an ideal gas, then the efficiency of the Otto cycle is

$$e = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}} \quad (22.5)$$

where γ is the ratio of the molar specific heats C_P/C_V for the fuel–air mixture and V_1/V_2 is the **compression ratio**. Equation 22.5, which we derive in Example 22.5, shows that the efficiency increases as the compression ratio increases. For a typical compression ratio of 8 and with $\gamma = 1.4$, we predict a theoretical efficiency of 56% for an engine operating in the idealized Otto cycle. This value is much greater than that achieved in real engines (15% to 20%) because of such effects as friction, energy transfer by conduction through the cylinder walls, and incomplete combustion of the air–fuel mixture.

Diesel engines operate on a cycle similar to the Otto cycle but do not employ a spark plug. The compression ratio for a diesel engine is much greater than that

Efficiency of the Otto cycle

for a gasoline engine. Air in the cylinder is compressed to a very small volume, and, as a consequence, the cylinder temperature at the end of the compression stroke is very high. At this point, fuel is injected into the cylinder. The temperature is high enough for the fuel–air mixture to ignite without the assistance of a spark plug. Diesel engines are more efficient than gasoline engines because of their greater compression ratios and resulting higher combustion temperatures.

EXAMPLE 22.5 Efficiency of the Otto Cycle

Show that the thermal efficiency of an engine operating in an idealized Otto cycle (see Figs. 22.11 and 22.12) is given by Equation 22.5. Treat the working substance as an ideal gas.

Solution First, let us calculate the work done by the gas during each cycle. No work is done during processes $B \rightarrow C$ and $D \rightarrow A$. The work done by the gas during the adiabatic compression $A \rightarrow B$ is negative, and the work done by the gas during the adiabatic expansion $C \rightarrow D$ is positive. The value of the net work done equals the area of the shaded region bounded by the closed curve in Figure 22.12. Because the change in internal energy for one cycle is zero, we see from the first law that the net work done during one cycle equals the net energy flow through the system:

$$W = Q_h - Q_c$$

Because processes $B \rightarrow C$ and $D \rightarrow A$ take place at constant volume, and because the gas is ideal, we find from the definition of molar specific heat (Eq. 21.8) that

$$Q_h = nC_V(T_C - T_B) \quad \text{and} \quad Q_c = nC_V(T_D - T_A)$$

Using these expressions together with Equation 22.2, we obtain for the thermal efficiency

$$(1) \quad e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_D - T_A}{T_C - T_B}$$

We can simplify this expression by noting that processes $A \rightarrow B$ and $C \rightarrow D$ are adiabatic and hence obey the relationship $TV^{\gamma-1} = \text{constant}$, which we obtained in Example 22.2. For the two adiabatic processes, then,

$$A \rightarrow B: \quad T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1}$$

$$C \rightarrow D: \quad T_C V_C^{\gamma-1} = T_D V_D^{\gamma-1}$$

Using these equations and relying on the fact that

$V_A = V_D = V_1$ and $V_B = V_C = V_2$, we find that

$$(2) \quad T_A V_1^{\gamma-1} = T_B V_2^{\gamma-1} \quad T_A = T_B \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

$$(3) \quad T_D V_1^{\gamma-1} = T_C V_2^{\gamma-1} \quad T_D = T_C \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

Subtracting (2) from (3) and rearranging, we find that

$$(4) \quad \frac{T_D - T_A}{T_C - T_B} = \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

Substituting (4) into (1), we obtain for the thermal efficiency

$$(5) \quad e = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}}$$

which is Equation 22.5.

We can also express this efficiency in terms of temperatures by noting from (2) and (3) that

$$\left(\frac{V_2}{V_1} \right)^{\gamma-1} = \frac{T_A}{T_B} = \frac{T_D}{T_C}$$

Therefore, (5) becomes

$$(6) \quad e = 1 - \frac{T_A}{T_B} = 1 - \frac{T_D}{T_C}$$

During the Otto cycle, the lowest temperature is T_A and the highest temperature is T_C . Therefore, the efficiency of a Carnot engine operating between reservoirs at these two temperatures, which is given by the expression $e_C = 1 - (T_A/T_C)$, is *greater* than the efficiency of the Otto cycle given by (6), as expected.

APPLICATION Models of Gasoline and Diesel Engines

We can use the thermodynamic principles discussed in this and earlier chapters to model the performance of gasoline and diesel engines. In both types of engine, a gas is first compressed in the cylinders of the engine and then the fuel–air mixture is ignited. Work is done on the gas during compression, but significantly more work is done on the piston by the

mixture as the products of combustion expand in the cylinder. The power of the engine is transferred from the piston to the crankshaft by the connecting rod.

Two important quantities of either engine are the **displacement volume**, which is the volume displaced by the piston as it moves from the bottom to the top of the cylinder, and the com-

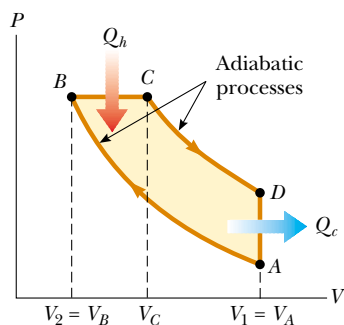


Figure 22.13 PV diagram for an ideal diesel engine.

pression ratio r , which is the ratio of the maximum and minimum volumes of the cylinder (see p. 680). In our notation, $r = V_A/V_B$, or V_1/V_2 in Eq. 22.5. Most gasoline and diesel engines operate with a four-cycle process (intake, compression, power, exhaust), in which the net work of the intake and exhaust cycles can be considered negligible. Therefore, power is developed only once for every two revolutions of the crankshaft.

In a diesel engine, only air (and no fuel) is present in the cylinder at the beginning of the compression. In the idealized diesel cycle of Figure 22.13, air in the cylinder undergoes an adiabatic compression from A to B. Starting at B, fuel is injected into the cylinder in such a way that the fuel–air mixture undergoes a constant-pressure expansion to an intermediate volume V_C ($B \rightarrow C$). The high temperature of the mixture causes combustion, and the power stroke is an adiabatic expansion back to $V_D = V_A$ ($C \rightarrow D$). The exhaust valve is opened, and a constant-volume output of energy occurs ($D \rightarrow A$) as the cylinder empties.

To simplify our calculations, we assume that the mixture in the cylinder is air modeled as an ideal gas. We use specific heats c instead of molar specific heats C and assume constant values for air at 300 K. We express the specific heats and the universal gas constant in terms of unit masses rather than moles. Thus, $c_V = 0.718 \text{ kJ/kg} \cdot \text{K}$, $c_P = 1.005 \text{ kJ/kg} \cdot \text{K}$, $\gamma = c_P/c_V = 1.40$, and $R = c_P - c_V = 0.287 \text{ kJ/kg} \cdot \text{K} = 0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}$.

A 3.00-L Gasoline Engine

Let us calculate the power delivered by a six-cylinder gasoline engine that has a displacement volume of 3.00 L operating at 4 000 rpm and having a compression ratio of $r = 9.50$. The air–fuel mixture enters a cylinder at atmospheric pressure and an ambient temperature of 27°C . During combustion, the mixture reaches a temperature of $1\,350^\circ\text{C}$.

First, let us calculate the work done by an individual cylinder. Using the initial pressure $P_A = 100 \text{ kPa}$ and the initial temperature $T_A = 300 \text{ K}$, we calculate the initial volume and the mass of the air–fuel mixture. We know that the ratio of the initial and final volumes is the compression ratio,

$$\frac{V_A}{V_B} = r = 9.50$$

We also know that the difference in volumes is the displacement volume. The 3.00-L rating of the engine is the total displacement volume for all six cylinders. Thus, for one cylinder,

$$V_A - V_B = \frac{3.00 \text{ L}}{6} = \frac{3.00 \times 10^{-3} \text{ m}^3}{6} = 0.500 \times 10^{-3} \text{ m}^3$$

Solving these two equations simultaneously, we find the initial and final volumes:

$$V_A = 0.559 \times 10^{-3} \text{ m}^3 \quad V_B = 0.588 \times 10^{-4} \text{ m}^3$$

Using the ideal gas law (in the form $PV = mRT$, because we are using the universal gas constant in terms of mass rather than moles), we can find the mass of the air–fuel mixture:

$$\begin{aligned} m &= \frac{P_A V_A}{RT_A} = \frac{(100 \text{ kPa})(0.559 \times 10^{-3} \text{ m}^3)}{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(300 \text{ K})} \\ &= 6.49 \times 10^{-4} \text{ kg} \end{aligned}$$

Process $A \rightarrow B$ (see Fig. 22.12) is an adiabatic compression, and this means that $PV^\gamma = \text{constant}$; hence,

$$\begin{aligned} P_B V_B^\gamma &= P_A V_A^\gamma \\ P_B &= P_A \left(\frac{V_A}{V_B} \right)^\gamma = P_A (r)^\gamma = (100 \text{ kPa})(9.50)^{1.40} \\ &= 2.34 \times 10^3 \text{ kPa} \end{aligned}$$

Using the ideal gas law, we find that the temperature after the compression is

$$\begin{aligned} T_B &= \frac{P_B V_B}{mR} = \frac{(2.34 \times 10^3 \text{ kPa})(0.588 \times 10^{-4} \text{ m}^3)}{(6.49 \times 10^{-4} \text{ kg})(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})} \\ &= 739 \text{ K} \end{aligned}$$

In process $B \rightarrow C$, the combustion that transforms the internal energy in chemical bonds into internal energy of molecular motion occurs at constant volume; thus, $V_C = V_B$. Combustion causes the temperature to increase to $T_C = 1\,350^\circ\text{C} = 1\,623 \text{ K}$. Using this value and the ideal gas law, we can calculate P_C :

$$\begin{aligned} P_C &= \frac{mRT_C}{V_C} \\ &= \frac{(6.49 \times 10^{-4} \text{ kg})(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(1\,623 \text{ K})}{(0.588 \times 10^{-4} \text{ m}^3)} \\ &= 5.14 \times 10^3 \text{ kPa} \end{aligned}$$

Process $C \rightarrow D$ is an adiabatic expansion; the pressure after the expansion is

$$\begin{aligned} P_D &= P_C \left(\frac{V_C}{V_D} \right)^\gamma = P_C \left(\frac{V_B}{V_A} \right)^\gamma = P_C \left(\frac{1}{r} \right)^\gamma \\ &= (5.14 \times 10^3 \text{ kPa}) \left(\frac{1}{9.50} \right)^{1.40} = 220 \text{ kPa} \end{aligned}$$

Using the ideal gas law again, we find the final temperature:

$$T_D = \frac{P_D V_D}{mR} = \frac{(220 \text{ kPa})(0.559 \times 10^{-3} \text{ m}^3)}{(6.49 \times 10^{-4} \text{ kg})(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})} = 660 \text{ K}$$

Now that we have the temperatures at the beginning and end of each process of the cycle, we can calculate the net energy transfer and net work done by each cylinder every two cycles. From Equation 21.8, we can state

$$\begin{aligned} Q_h &= Q_{\text{in}} = mc_V(T_C - T_B) \\ &= (6.49 \times 10^{-4} \text{ kg})(0.718 \text{ kJ/kg} \cdot \text{K})(1623 \text{ K} - 739 \text{ K}) \\ &= 0.412 \text{ kJ} \end{aligned}$$

$$\begin{aligned} Q_c &= Q_{\text{out}} = mc_V(T_D - T_A) \\ &= (6.49 \times 10^{-4} \text{ kg})(0.718 \text{ kJ/kg} \cdot \text{K})(660 \text{ K} - 300 \text{ K}) \\ &= 0.168 \text{ kJ} \end{aligned}$$

$$W_{\text{net}} = Q_{\text{in}} - Q_{\text{out}} = 0.244 \text{ kJ}$$

From Equation 22.2, the efficiency is $e = W_{\text{net}}/Q_{\text{in}} = 59\%$. (We can also use Equation 22.5 to calculate the efficiency directly from the compression ratio.)

Recalling that power is delivered every other revolution of the crankshaft, we find that the net power for the six-cylinder engine operating at 4 000 rpm is

$$\begin{aligned} \mathcal{P}_{\text{net}} &= 6 \left(\frac{1}{2 \text{ rev}} \right) (4000 \text{ rev/min}) (1 \text{ min}/60 \text{ s}) (0.244 \text{ kJ}) \\ &= 49 \text{ kW} = 66 \text{ hp} \end{aligned}$$

A 2.00-L Diesel Engine

Let us calculate the power delivered by a four-cylinder diesel engine that has a displacement volume of 2.00 L and is operating at 3 000 rpm. The compression ratio is $r = V_A/V_B = 22.0$, and the **cutoff ratio**, which is the ratio of the volume change during the constant-pressure process $B \rightarrow C$ in Figure 22.13, is $r_c = V_C/V_B = 2.00$. The air enters each cylinder at the beginning of the compression cycle at atmospheric pressure and at an ambient temperature of 27°C.

Our model of the diesel engine is similar to our model of the gasoline engine except that now the fuel is injected at point B and the mixture self-ignites near the end of the compression cycle $A \rightarrow B$, when the temperature reaches the ignition temperature. We assume that the energy input occurs in the constant-pressure process $B \rightarrow C$, and that the expansion process continues from C to D with no further energy transfer by heat.

Let us calculate the work done by an individual cylinder that has an initial volume of $V_A = (2.00 \times 10^{-3} \text{ m}^3)/4 = 0.500 \times 10^{-3} \text{ m}^3$. Because the compression ratio is quite high, we approximate the maximum cylinder volume to be the displacement volume. Using the initial pressure $P_A = 100 \text{ kPa}$ and initial temperature $T_A = 300 \text{ K}$, we can calculate the mass of the air in the cylinder using the ideal gas law:

$$m = \frac{P_A V_A}{RT_A} = \frac{(100 \text{ kPa})(0.500 \times 10^{-3} \text{ m}^3)}{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(300 \text{ K})} = 5.81 \times 10^{-4} \text{ kg}$$

Process $A \rightarrow B$ is an adiabatic compression, so $PV^\gamma = \text{constant}$; thus,

$$\begin{aligned} P_B V_B^\gamma &= P_A V_A^\gamma \\ P_B &= P_A \left(\frac{V_A}{V_B} \right)^\gamma = (100 \text{ kPa})(22.0)^{1.40} = 7.57 \times 10^3 \text{ kPa} \end{aligned}$$

Using the ideal gas law, we find that the temperature of the air after the compression is

$$\begin{aligned} T_B &= \frac{P_B V_B}{mR} = \frac{(7.57 \times 10^3 \text{ kPa})(0.500 \times 10^{-3} \text{ m}^3)}{(5.81 \times 10^{-4} \text{ kg})(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})} \left(\frac{1}{22.0} \right) \\ &= 1.03 \times 10^3 \text{ K} \end{aligned}$$

Process $B \rightarrow C$ is a constant-pressure expansion; thus, $P_C = P_B$. We know from the cutoff ratio of 2.00 that the volume doubles in this process. According to the ideal gas law, a doubling of volume in an isobaric process results in a doubling of the temperature, so

$$T_C = 2T_B = 2.06 \times 10^3 \text{ K}$$

Process $C \rightarrow D$ is an adiabatic expansion; therefore,

$$\begin{aligned} P_D &= P_C \left(\frac{V_C}{V_D} \right)^\gamma = P_C \left(\frac{V_C}{V_B} \frac{V_B}{V_D} \right)^\gamma = P_C \left(r_c \frac{1}{r} \right)^\gamma \\ &= (7.57 \times 10^3 \text{ kPa}) \left(\frac{2.00}{22.0} \right)^{1.40} = 264 \text{ kPa} \end{aligned}$$

We find the temperature at D from the ideal gas law:

$$\begin{aligned} T_D &= \frac{P_D V_D}{mR} = \frac{(264 \text{ kPa})(0.500 \times 10^{-3} \text{ m}^3)}{(5.81 \times 10^{-4} \text{ kg})(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})} \\ &= 792 \text{ K} \end{aligned}$$

Now that we have the temperatures at the beginning and the end of each process, we can calculate the net energy transfer by heat and the net work done by each cylinder every two cycles:

$$\begin{aligned} Q_h &= Q_{\text{in}} = mc_P(T_C - T_B) = 0.601 \text{ kJ} \\ Q_c &= Q_{\text{out}} = mc_V(T_D - T_A) = 0.205 \text{ kJ} \\ W_{\text{net}} &= Q_{\text{in}} - Q_{\text{out}} = 0.396 \text{ kJ} \end{aligned}$$

The efficiency is $e = W_{\text{net}}/Q_{\text{in}} = 66\%$.

The net power for the four-cylinder engine operating at 3 000 rpm is

$$\begin{aligned} \mathcal{P}_{\text{net}} &= 4 \left(\frac{1}{2 \text{ rev}} \right) (3000 \text{ rev/min}) (1 \text{ min}/60 \text{ s}) (0.396 \text{ kJ}) \\ &= 39.6 \text{ kW} = 53 \text{ hp} \end{aligned}$$

Of course, modern engine design goes beyond this simple thermodynamic treatment, which uses idealized cycles.

22.5 HEAT PUMPS AND REFRIGERATORS

In Section 22.1 we introduced a heat pump as a mechanical device that moves energy from a region at lower temperature to a region at higher temperature. Heat pumps have long been used for cooling homes and buildings, and they are now becoming increasingly popular for heating them as well. The heat pump contains two sets of metal coils that can exchange energy by heat with the surroundings: one set on the outside of the building, in contact with the air or buried in the ground; and the other set in the interior of the building. In the heating mode, a circulating fluid flowing through the coils absorbs energy from the outside and releases it to the interior of the building from the interior coils. The fluid is cold and at low pressure when it is in the external coils, where it absorbs energy by heat from either the air or the ground. The resulting warm fluid is then compressed and enters the interior coils as a hot, high-pressure fluid, where it releases its stored energy to the interior air.



An air conditioner is simply a heat pump operating in the cooling mode, with its exterior and interior coils interchanged. Energy is absorbed into the circulating fluid in the interior coils; then, after the fluid is compressed, energy leaves the fluid through the external coils. The air conditioner must have a way to release energy to the outside. Otherwise, the work done on the air conditioner would represent energy added to the air inside the house, and the temperature would increase. In the same manner, a refrigerator cannot cool the kitchen if the refrigerator door is left open. The amount of energy leaving the external coils (Fig. 22.14) behind or underneath the refrigerator is greater than the amount of energy removed from the food or from the air in the kitchen if the door is left open. The difference between the energy out and the energy in is the work done by the electricity supplied to the refrigerator.

Figure 22.15 is a schematic representation of a heat pump. The cold temperature is T_c , the hot temperature is T_h , and the energy absorbed by the circulating fluid is Q_c . The heat pump does work W on the fluid, and the energy transferred from the pump to the building in the heating mode is Q_h .

The effectiveness of a heat pump is described in terms of a number called the **coefficient of performance** (COP). In the heating mode, the COP is defined as the ratio of the energy transferred to the hot reservoir to the work required to transfer that energy:

$$\text{COP (heating mode)} \equiv \frac{\text{Energy transferred at high temperature}}{\text{Work done by pump}} = \frac{Q_h}{W} \quad (22.6)$$

Note that the COP is similar to the thermal efficiency for a heat engine in that it is a ratio of what you get (energy delivered to the interior of the building) to what you give (work input). Because Q_h is generally greater than W , typical values for the COP are greater than unity. It is desirable for the COP to be as high as possible, just as it is desirable for the thermal efficiency of an engine to be as high as possible.

If the outside temperature is 25°F or higher, then the COP for a heat pump is about 4. That is, the amount of energy transferred to the building is about four times greater than the work done by the motor in the heat pump. However, as the outside temperature decreases, it becomes more difficult for the heat pump to extract sufficient energy from the air, and so the COP decreases. In fact, the COP can fall below unity for temperatures below the midteens. Thus, the use of heat pumps that extract energy from the air, while satisfactory in moderate climates, is not appropriate in areas where winter temperatures are very low. It is possible to



Figure 22.14 The coils on the back of a refrigerator transfer energy by heat to the air. The second law of thermodynamics states that this amount of energy must be greater than the amount of energy removed from the contents of the refrigerator (or from the air in the kitchen, if the refrigerator door is left open).

use heat pumps in colder areas by burying the external coils deep in the ground. In this case, the energy is extracted from the ground, which tends to be warmer than the air in the winter.

Quick Quiz 22.1

In an electric heater, electrical energy can be converted to internal energy with an efficiency of 100%. By what percentage does the cost of heating your home change when you replace your electric heating system with a heat pump that has a COP of 4? Assume that the motor running the heat pump is 100% efficient.

Theoretically, a Carnot-cycle heat engine run in reverse constitutes the most effective heat pump possible, and it determines the maximum COP for a given combination of hot and cold reservoir temperatures. Using Equations 22.1 and 22.3, we see that the maximum COP for a heat pump in its heating mode is

$$\begin{aligned}\text{COP}_C(\text{heating mode}) &= \frac{Q_h}{W} \\ &= \frac{Q_h}{Q_h - Q_c} = \frac{1}{1 - \frac{Q_c}{Q_h}} = \frac{1}{1 - \frac{T_c}{T_h}} = \frac{T_h}{T_h - T_c}\end{aligned}$$

For a heat pump operating in the cooling mode, “what you get” is energy removed from the cold reservoir. The most effective refrigerator or air conditioner is one that removes the greatest amount of energy from the cold reservoir in exchange for the least amount of work. Thus, for these devices we define the COP in terms of Q_c :

$$\text{COP (cooling mode)} = \frac{Q_c}{W} \quad (22.7)$$

A good refrigerator should have a high COP, typically 5 or 6.

The greatest possible COP for a heat pump in the cooling mode is that of a heat pump whose working substance is carried through a Carnot cycle in reverse:

$$\text{COP}_C(\text{cooling mode}) = \frac{T_c}{T_h - T_c}$$

As the difference between the temperatures of the two reservoirs approaches zero in this expression, the theoretical COP approaches infinity. In practice, the low temperature of the cooling coils and the high temperature at the compressor limit the COP to values below 10.

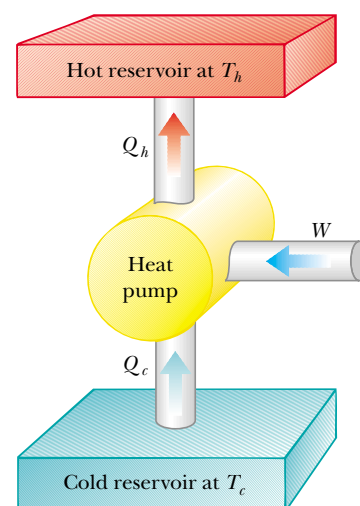


Figure 22.15 Schematic diagram of a heat pump, which absorbs energy Q_c from a cold reservoir and expels energy Q_h to a hot reservoir. Note that this diagram is the same as that for the refrigerator shown in Figure 22.5.

QuickLab

Estimate the COP of your refrigerator by making rough temperature measurements of the stored food and of the exhaust coils (found either on the back of the unit or behind a panel on the bottom). Use just your hand if no thermometer is available.

22.6 ENTROPY

The zeroth law of thermodynamics involves the concept of temperature, and the first law involves the concept of internal energy. Temperature and internal energy are both state functions—that is, they can be used to describe the thermodynamic state of a system. Another state function—this one related to the second law of thermodynamics—is **entropy** S . In this section we define entropy on a macroscopic scale as it was first expressed by Clausius in 1865.

Consider any infinitesimal process in which a system changes from one equilibrium state to another. If dQ_r is the amount of energy transferred by heat when the system follows a reversible path between the states, then the change in entropy dS is equal to this amount of energy for the reversible process divided by the absolute temperature of the system:

Clausius definition of change in entropy

$$dS = \frac{dQ_r}{T} \quad (22.8)$$

We have assumed that the temperature is constant because the process is infinitesimal. Since we have claimed that entropy is a state function, **the change in entropy during a process depends only on the end points and therefore is independent of the actual path followed.**

The subscript r on the quantity dQ_r is a reminder that the transferred energy is to be measured along a reversible path, even though the system may actually have followed some irreversible path. When energy is absorbed by the system, dQ_r is positive and the entropy of the system increases. When energy is expelled by the system, dQ_r is negative and the entropy of the system decreases. Note that Equation 22.8 defines not entropy but rather the *change* in entropy. Hence, the meaningful quantity in describing a process is the *change* in entropy.

Entropy was originally formulated as a useful concept in thermodynamics; however, its importance grew tremendously as the field of statistical mechanics developed because the analytical techniques of statistical mechanics provide an alternative means of interpreting entropy. In statistical mechanics, the behavior of a substance is described in terms of the statistical behavior of its atoms and molecules. One of the main results of this treatment is that **isolated systems tend toward disorder and that entropy is a measure of this disorder.** For example, consider the molecules of a gas in the air in your room. If half of the gas molecules had velocity vectors of equal magnitude directed toward the left and the other half had velocity vectors of the same magnitude directed toward the right, the situation would be very ordered. However, such a situation is extremely unlikely. If you could actually view the molecules, you would see that they move haphazardly in all directions, bumping into one another, changing speed upon collision, some going fast and others going slowly. This situation is highly disordered.

The cause of the tendency of an isolated system toward disorder is easily explained. To do so, we distinguish between *microstates* and *macrostates* of a system. A **microstate** is a particular description of the properties of the individual molecules of the system. For example, the description we just gave of the velocity vectors of the air molecules in your room being very ordered refers to a particular microstate, and the more likely haphazard motion is another microstate—one that represents disorder. A **macrostate** is a description of the conditions of the system from a macroscopic point of view and makes use of macroscopic variables such as pressure, density, and temperature. For example, in both of the microstates described for the air molecules in your room, the air molecules are distributed uniformly throughout the volume of the room; this uniform density distribution is a macrostate. We could not distinguish between our two microstates by making a macroscopic measurement—both microstates would appear to be the same macroscopically, and the two macrostates corresponding to these microstates are equivalent.

For any given macrostate of the system, a number of microstates are possible, or *accessible*. Among these microstates, it is assumed that all are equally probable. However, when all possible microstates are examined, it is found that far more of them are disordered than are ordered. Because all of the microstates are equally

probable, it is highly likely that the actual macrostate is one resulting from one of the highly disordered microstates, simply because there are many more of them. Similarly, the probability of a macrostate's forming from disordered microstates is greater than the probability of a macrostate's forming from ordered microstates.

All physical processes that take place in a system tend to cause the system and its surroundings to move toward more probable macrostates. The more probable macrostate is always one of greater disorder. If we consider a system and its surroundings to include the entire Universe, then the Universe is always moving toward a macrostate corresponding to greater disorder. Because entropy is a measure of disorder, an alternative way of stating this is **the entropy of the Universe increases in all real processes**. This is yet another statement of the second law of thermodynamics that can be shown to be equivalent to the Kelvin–Planck and Clausius statements.

To calculate the change in entropy for a finite process, we must recognize that T is generally not constant. If dQ_r is the energy transferred by heat when the system is at a temperature T , then the change in entropy in an arbitrary reversible process between an initial state and a final state is

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T} \quad (\text{reversible path}) \quad (22.9)$$

As with an infinitesimal process, the change in entropy ΔS of a system going from one state to another has the same value for *all* paths connecting the two states. That is, the finite change in entropy ΔS of a system depends only on the properties of the initial and final equilibrium states. Thus, we are free to choose a particular reversible path over which to evaluate the entropy in place of the actual path, as long as the initial and final states are the same for both paths.

In real processes, the disorder of the Universe increases

Change in entropy for a finite process

Quick Quiz 22.2

Which of the following is true for the entropy change of a system that undergoes a reversible, adiabatic process? (a) $\Delta S < 0$. (b) $\Delta S = 0$. (c) $\Delta S > 0$.

Let us consider the changes in entropy that occur in a Carnot heat engine operating between the temperatures T_c and T_h . In one cycle, the engine absorbs energy Q_h from the hot reservoir and expels energy Q_c to the cold reservoir. These energy transfers occur only during the isothermal portions of the Carnot cycle; thus, the constant temperature can be brought out in front of the integral sign in Equation 22.9. The integral then simply has the value of the total amount of energy transferred by heat. Thus, the total change in entropy for one cycle is

$$\Delta S = \frac{Q_h}{T_h} - \frac{Q_c}{T_c}$$

where the negative sign represents the fact that energy Q_c is expelled by the system, since we continue to define Q_c as a positive quantity when referring to heat engines. In Example 22.2 we showed that, for a Carnot engine,

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

Using this result in the previous expression for ΔS , we find that the total change in

The change in entropy for a Carnot cycle is zero

entropy for a Carnot engine operating in a cycle is *zero*:

$$\Delta S = 0$$

Now let us consider a system taken through an arbitrary (non-Carnot) reversible cycle. Because entropy is a state function—and hence depends only on the properties of a given equilibrium state—we conclude that $\Delta S = 0$ for *any* reversible cycle. In general, we can write this condition in the mathematical form

$\Delta S = 0$ for any reversible cycle

$$\oint \frac{dQ_r}{T} = 0 \quad (22.10)$$

where the symbol \oint indicates that the integration is over a closed path.

Quasi-Static, Reversible Process for an Ideal Gas

Let us suppose that an ideal gas undergoes a quasi-static, reversible process from an initial state having temperature T_i and volume V_i to a final state described by T_f and V_f . Let us calculate the change in entropy of the gas for this process.

Writing the first law of thermodynamics in differential form and rearranging the terms, we have $dQ_r = dE_{\text{int}} + dW$, where $dW = P dV$. For an ideal gas, recall that $dE_{\text{int}} = nC_V dT$ (Eq. 21.12), and from the ideal gas law, we have $P = nRT/V$. Therefore, we can express the energy transferred by heat in the process as

$$dQ_r = dE_{\text{int}} + P dV = nC_V dT + nRT \frac{dV}{V}$$

We cannot integrate this expression as it stands because the last term contains two variables, T and V . However, if we divide all terms by T , each of the terms on the right-hand side depends on only one variable:

$$\frac{dQ_r}{T} = nC_V \frac{dT}{T} + nR \frac{dV}{V} \quad (22.11)$$

Assuming that C_V is constant over the interval in question, and integrating Equation 22.11 from the initial state to the final state, we obtain

$$\Delta S = \int_i^f \frac{dQ_r}{T} = nC_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i} \quad (22.12)$$

This expression demonstrates mathematically what we argued earlier—that ΔS depends only on the initial and final states and is independent of the path between the states. Also, note in Equation 22.12 that ΔS can be positive or negative, depending on the values of the initial and final volumes and temperatures. Finally, for a cyclic process ($T_i = T_f$ and $V_i = V_f$), we see from Equation 22.12 that $\Delta S = 0$. This is evidence that entropy is a state function.

EXAMPLE 22.6 Change in Entropy—Melting

A solid that has a latent heat of fusion L_f melts at a temperature T_m . (a) Calculate the change in entropy of this substance when a mass m of the substance melts.

Solution Let us assume that the melting occurs so slowly that it can be considered a reversible process. In this case the temperature can be regarded as constant and equal to T_m .

Making use of Equations 22.9 and that for the latent heat of fusion $Q = mL_f$ (Eq. 20.6), we find that

$$\Delta S = \int \frac{dQ_r}{T} = \frac{1}{T_m} \int dQ = \frac{Q}{T_m} = \frac{mL_f}{T_m}$$

Note that we are able to remove T_m from the integral because the process is isothermal. Note also that ΔS is positive. This means that when a solid melts, its entropy increases because the molecules are much more disordered in the liquid state than they are in the solid state. The positive value for ΔS also means that the substance in its liquid state does not spontaneously transfer energy from itself to the surroundings and freeze because to do so would involve a spontaneous decrease in entropy.

(b) Estimate the value of the change in entropy of an ice cube when it melts.

Solution Let us assume an ice tray makes cubes that are about 3 cm on a side. The volume per cube is then (very roughly) 30 cm^3 . This much liquid water has a mass of 30 g. From Table 20.2 we find that the latent heat of fusion of ice is $3.33 \times 10^5 \text{ J/kg}$. Substituting these values into our answer for part (a), we find that

$$\Delta S = \frac{mL_f}{T_m} = \frac{(0.03 \text{ kg})(3.33 \times 10^5 \text{ J/kg})}{273 \text{ K}} = 4 \times 10^1 \text{ J/K}$$

We retain only one significant figure, in keeping with the nature of our estimations.

22.7 ENTROPY CHANGES IN IRREVERSIBLE PROCESSES

By definition, calculation of the change in entropy requires information about a reversible path connecting the initial and final equilibrium states. To calculate changes in entropy for real (irreversible) processes, we must remember that entropy (like internal energy) depends only on the *state* of the system. That is, entropy is a state function. Hence, the change in entropy when a system moves between any two equilibrium states depends only on the initial and final states. We can show that if this were not the case, the second law of thermodynamics would be violated.

We now calculate the entropy change in some irreversible process between two equilibrium states by devising a reversible process (or series of reversible processes) between the same two states and computing $\Delta S = \int dQ_r/T$ for the reversible process. In irreversible processes, it is critically important that we distinguish between Q , the actual energy transfer in the process, and Q_r , the energy that would have been transferred by heat along a reversible path. Only Q_r is the correct value to be used in calculating the entropy change.

As we shall see in the following examples, the change in entropy for a system and its surroundings is always positive for an irreversible process. In general, the total entropy—and therefore the disorder—always increase in an irreversible process. Keeping these considerations in mind, we can state the second law of thermodynamics as follows:

The total entropy of an isolated system that undergoes a change can never decrease.

Furthermore, **if the process is irreversible, then the total entropy of an isolated system always increases. In a reversible process, the total entropy of an isolated system remains constant.**

When dealing with a system that is not isolated from its surroundings, remember that the increase in entropy described in the second law is that of the system *and* its surroundings. When a system and its surroundings interact in an irreversible process, the increase in entropy of one is greater than the decrease in entropy of the other. Hence, we conclude that **the change in entropy of the Universe must be greater than zero for an irreversible process and equal to zero for a reversible process.** Ultimately, the entropy of the Universe should reach a maximum value. At this value, the Universe will be in a state of uniform temperature and density. All physical, chemical, and biological processes will cease because a state of perfect disorder implies that no energy is available for doing work. This gloomy state of affairs is sometimes referred to as the heat death of the Universe.

Quick Quiz 22.3

In the presence of sunlight, a tree rearranges an unorganized collection of carbon dioxide and water molecules into the highly ordered collection of molecules we see as leaves and branches. True or false: This reduction of entropy in the tree is a violation of the second law of thermodynamics. Explain your response.

Entropy Change in Thermal Conduction

Let us now consider a system consisting of a hot reservoir and a cold reservoir in thermal contact with each other and isolated from the rest of the Universe. A process occurs during which energy Q is transferred by heat from the hot reservoir at temperature T_h to the cold reservoir at temperature T_c . Because the cold reservoir absorbs energy Q , its entropy increases by Q/T_c . At the same time, the hot reservoir loses energy Q , and so its entropy change is $-Q/T_h$. Because $T_h > T_c$, the increase in entropy of the cold reservoir is greater than the decrease in entropy of the hot reservoir. Therefore, the change in entropy of the system (and of the Universe) is greater than zero:

$$\Delta S_U = \frac{Q}{T_c} + \frac{-Q}{T_h} > 0$$

EXAMPLE 22.7 Which Way Does the Energy Flow?

A large, cold object is at 273 K, and a large, hot object is at 373 K. Show that it is impossible for a small amount of energy—for example, 8.00 J—to be transferred spontaneously from the cold object to the hot one without a decrease in the entropy of the Universe and therefore a violation of the second law.

Solution We assume that, during the energy transfer, the two objects do not undergo a temperature change. This is not a necessary assumption; we make it only to avoid using integral calculus in our calculations. The process as described is irreversible, and so we must find an equivalent reversible process. It is sufficient to assume that the objects are connected by a poor thermal conductor whose temperature spans the range from 273 K to 373 K. This conductor transfers energy slowly, and its state does not change during the process. Under this assumption, the energy transfer to or from each object is reversible, and we may set $Q = Q_r$. The entropy change of the hot object is

$$\Delta S_h = \frac{Q_r}{T_h} = \frac{8.00 \text{ J}}{373 \text{ K}} = 0.0214 \text{ J/K}$$

The cold object loses energy, and its entropy change is

$$\Delta S_c = \frac{Q_r}{T_c} = \frac{-8.00 \text{ J}}{273 \text{ K}} = -0.0293 \text{ J/K}$$

We consider the two objects to be isolated from the rest of the Universe. Thus, the entropy change of the Universe is just

that of our two-object system, which is

$$\Delta S_U = \Delta S_c + \Delta S_h = -0.0079 \text{ J/K}$$

This decrease in entropy of the Universe is in violation of the second law. That is, **the spontaneous transfer of energy from a cold to a hot object cannot occur.**

In terms of disorder, let us consider the violation of the second law if energy were to continue to transfer spontaneously from a cold object to a hot object. Before the transfer, a certain degree of order is associated with the different temperatures of the objects. The hot object's molecules have a higher average energy than the cold object's molecules. If energy spontaneously flows from the cold object to the hot object, then, over a period of time, the cold object will become colder and the hot object will become hotter. The difference in average molecular energy will become even greater; this would represent an increase in order for the system and a violation of the second law.

In comparison, the process that does occur naturally is the flow of energy from the hot object to the cold object. In this process, the difference in average molecular energy decreases; this represents a more random distribution of energy and an increase in disorder.

Exercise Suppose that 8.00 J of energy is transferred from a hot object to a cold one. What is the net entropy change of the Universe?

Answer +0.0079 J/K.

Entropy Change in a Free Expansion

Let us again consider the adiabatic free expansion of a gas occupying an initial volume V_i (Fig. 22.16). A membrane separating the gas from an evacuated region is broken, and the gas expands (irreversibly) to a volume V_f . Let us find the changes in entropy of the gas and of the Universe during this process.

The process is clearly neither reversible nor quasi-static. The work done by the gas against the vacuum is zero, and because the walls are insulating, no energy is transferred by heat during the expansion. That is, $W = 0$ and $Q = 0$. Using the first law, we see that the change in internal energy is zero. Because the gas is ideal, E_{int} depends on temperature only, and we conclude that $\Delta T = 0$ or $T_i = T_f$.

To apply Equation 22.9, we cannot use $Q = 0$, the value for the irreversible process, but must instead find Q_r ; that is, we must find an equivalent reversible path that shares the same initial and final states. A simple choice is an isothermal, reversible expansion in which the gas pushes slowly against a piston while energy enters the gas by heat from a reservoir at the temperature constant. Because T is constant in this process, Equation 22.9 gives

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \frac{1}{T} \int_i^f dQ_r$$

For an isothermal process, the first law of thermodynamics specifies that $\int_i^f dQ_r$ is equal to the work done by the gas during the expansion from V_i to V_f , which is given by Equation 20.13. Using this result, we find that the entropy change for the gas is

$$\Delta S = nR \ln \frac{V_f}{V_i} \quad (22.13)$$

Because $V_f > V_i$, we conclude that ΔS is positive. This positive result indicates that both the entropy and the disorder of the gas increase as a result of the irreversible, adiabatic expansion.

Because the free expansion takes place in an insulated container, no energy is transferred by heat from the surroundings. (Remember that the isothermal, reversible expansion is only a *replacement* process that we use to calculate the entropy change for the gas; it is not the *actual* process.) Thus, the free expansion has no effect on the surroundings, and the entropy change of the surroundings is zero. Thus, the entropy change for the Universe is positive; this is consistent with the second law.

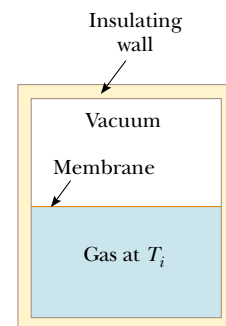


Figure 22.16 Adiabatic free expansion of a gas. When the membrane separating the gas from the evacuated region is ruptured, the gas expands freely and irreversibly. As a result, it occupies a greater final volume. The container is thermally insulated from its surroundings; thus, $Q = 0$.

EXAMPLE 22.8 Free Expansion of a Gas

Calculate the change in entropy for a process in which 2.00 mol of an ideal gas undergoes a free expansion to three times its initial volume.

Solution Using Equation 22.13 with $n = 2.00$ mol and $V_f = 3V_i$, we find that

$$\Delta S = nR \ln \frac{V_f}{V_i} = (2.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(\ln 3)$$

$$= 18.3 \text{ J/K}$$

It is easy to see that the gas is more disordered after the expansion. Instead of being concentrated in a relatively small space, the molecules are scattered over a larger region.

Entropy Change in Calorimetric Processes

A substance of mass m_1 , specific heat c_1 , and initial temperature T_1 is placed in thermal contact with a second substance of mass m_2 , specific heat c_2 , and initial

temperature $T_2 > T_1$. The two substances are contained in a calorimeter so that no energy is lost to the surroundings. The system of the two substances is allowed to reach thermal equilibrium. What is the total entropy change for the system?

First, let us calculate the final equilibrium temperature T_f . Using the techniques of Section 20.2—namely, Equation 20.5, $Q_{\text{cold}} = -Q_{\text{hot}}$, and Equation 20.4, $Q = mc\Delta T$, we obtain

$$\begin{aligned} m_1 c_1 \Delta T_1 &= -m_2 c_2 \Delta T_2 \\ m_1 c_1 (T_f - T_1) &= -m_2 c_2 (T_f - T_2) \end{aligned}$$

Solving for T_f , we have

$$T_f = \frac{m_1 c_1 T_1 + m_2 c_2 T_2}{m_1 c_1 + m_2 c_2} \quad (22.14)$$

The process is irreversible because the system goes through a series of non-equilibrium states. During such a transformation, the temperature of the system at any time is not well defined because different parts of the system have different temperatures. However, we can imagine that the hot substance at the initial temperature T_2 is slowly cooled to the temperature T_f as it comes into contact with a series of reservoirs differing infinitesimally in temperature, the first reservoir being at T_2 and the last being at T_f . Such a series of very small changes in temperature would approximate a reversible process. We imagine doing the same thing for the cold substance. Applying Equation 22.9 and noting that $dQ = mc\,dT$ for an infinitesimal change, we have

$$\Delta S = \int_1 \frac{dQ_{\text{cold}}}{T} + \int_2 \frac{dQ_{\text{hot}}}{T} = m_1 c_1 \int_{T_1}^{T_f} \frac{dT}{T} + m_2 c_2 \int_{T_2}^{T_f} \frac{dT}{T}$$

where we have assumed that the specific heats remain constant. Integrating, we find that

$$\Delta S = m_1 c_1 \ln \frac{T_f}{T_1} + m_2 c_2 \ln \frac{T_f}{T_2} \quad (22.15)$$

where T_f is given by Equation 22.14. If Equation 22.14 is substituted into Equation 22.15, we can show that one of the terms in Equation 22.15 is always positive and the other is always negative. (You may want to verify this for yourself.) The positive term is always greater than the negative term, and this results in a positive value for ΔS . Thus, we conclude that the entropy of the Universe increases in this irreversible process.

Finally, you should note that Equation 22.15 is valid only when no mixing of different substances occurs, because a further entropy increase is associated with the increase in disorder during the mixing. If the substances are liquids or gases and mixing occurs, the result applies only if the two fluids are identical, as in the following example.

Change in entropy for a calorimetric process

EXAMPLE 22.9 Calculating ΔS for a Calorimetric Process

Suppose that 1.00 kg of water at 0.00°C is mixed with an equal mass of water at 100°C. After equilibrium is reached, the mixture has a uniform temperature of 50.0°C. What is the change in entropy of the system?

Solution We can calculate the change in entropy from Equation 22.15 using the values $m_1 = m_2 = 1.00$ kg, $c_1 = c_2 = 4186$ J/kg·K, $T_1 = 273$ K, $T_2 = 373$ K, and $T_f = 323$ K:

$$\begin{aligned}\Delta S &= m_1 c_1 \ln \frac{T_f}{T_1} + m_2 c_2 \ln \frac{T_f}{T_2} \\ &= (1.00 \text{ kg})(4186 \text{ J/kg} \cdot \text{K}) \ln \left(\frac{323 \text{ K}}{273 \text{ K}} \right) \\ &\quad + (1.00 \text{ kg})(4186 \text{ J/kg} \cdot \text{K}) \ln \left(\frac{323 \text{ K}}{373 \text{ K}} \right) \\ &= 704 \text{ J/K} - 602 \text{ J/K} = 102 \text{ J/K}\end{aligned}$$

That is, as a result of this irreversible process, the increase in entropy of the cold water is greater than the decrease in entropy of the warm water. Consequently, the increase in entropy of the system is 102 J/K.

Optional Section

22.8 ENTROPY ON A MICROSCOPIC SCALE⁴

As we have seen, we can approach entropy by relying on macroscopic concepts and using parameters such as pressure and temperature. We can also treat entropy from a microscopic viewpoint through statistical analysis of molecular motions. We now use a microscopic model to investigate once again the free expansion of an ideal gas, which was discussed from a macroscopic point of view in the preceding section.

In the kinetic theory of gases, gas molecules are represented as particles moving randomly. Let us suppose that the gas is initially confined to a volume V_i , as shown in Figure 22.17a. When the partition separating V_i from a larger container is removed, the molecules eventually are distributed throughout the greater volume V_f (Fig. 22.17b). For a given uniform distribution of gas in the volume, there are a large number of equivalent microstates, and we can relate the entropy of the gas to the number of microstates corresponding to a given macrostate.

We count the number of microstates by considering the variety of molecular locations involved in the free expansion. The instant after the partition is removed (and before the molecules have had a chance to rush into the other half of the container), all the molecules are in the initial volume. We assume that each molecule occupies some microscopic volume V_m . The total number of possible locations of a single molecule in a macroscopic initial volume V_i is the ratio $w_i = V_i/V_m$, which is a huge number. We use w_i here to represent the number of ways that the molecule can be placed in the volume, or the number of microstates, which is equivalent to the number of available locations. We assume that the molecule's occupying each of these locations is equally probable.

As more molecules are added to the system, the number of possible ways that the molecules can be positioned in the volume multiplies. For example, in considering two molecules, for every possible placement of the first, all possible placements of the second are available. Thus, there are w_1 ways of locating the first molecule, and for each of these, there are w_2 ways of locating the second molecule. The total number of ways of locating the two molecules is $w_1 w_2$.

Neglecting the very small probability of having two molecules occupy the same location, each molecule may go into any of the V_i/V_m locations, and so the number of ways of locating N molecules in the volume becomes $W_i = w_i^N = (V_i/V_m)^N$. (W_i is not to be confused with work.) Similarly, when the volume is increased to V_f , the number of ways of locating N molecules increases to $W_f = w_f^N = (V_f/V_m)^N$. The ratio of the number of ways of placing the molecules in the volume for the

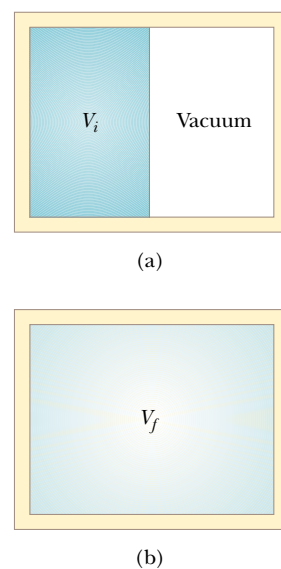


Figure 22.17 In a free expansion, the gas is allowed to expand into a region that was previously a vacuum.

⁴ This section was adapted from A. Hudson and R. Nelson, *University Physics*, Philadelphia, Saunders College Publishing, 1990.

initial and final configurations is

$$\frac{W_f}{W_i} = \frac{(V_f/V_m)^N}{(V_i/V_m)^N} = \left(\frac{V_f}{V_i}\right)^N$$

If we now take the natural logarithm of this equation and multiply by Boltzmann's constant, we find that

$$k_B \ln\left(\frac{W_f}{W_i}\right) = nN_A k_B \ln\left(\frac{V_f}{V_i}\right)$$

where we have used the equality $N = nN_A$. We know from Equation 19.11 that $N_A k_B$ is the universal gas constant R ; thus, we can write this equation as

$$k_B \ln W_f - k_B \ln W_i = nR \ln\left(\frac{V_f}{V_i}\right) \quad (22.16)$$

From Equation 22.13 we know that when n mol of a gas undergoes a free expansion from V_i to V_f , the change in entropy is

$$S_f - S_i = nR \ln\left(\frac{V_f}{V_i}\right) \quad (22.17)$$

Note that the right-hand sides of Equations 22.16 and 22.17 are identical. Thus, we make the following important connection between entropy and the number of microstates for a given macrostate:

Entropy (microscopic definition)

$$S \equiv k_B \ln W \quad (22.18)$$

The more microstates there are that correspond to a given macrostate, the greater is the entropy of that macrostate. As we have discussed previously, there are many more disordered microstates than ordered microstates. Thus, Equation 22.18 indicates mathematically that **entropy is a measure of microscopic disorder**. Although in our discussion we used the specific example of the free expansion of an ideal gas, a more rigorous development of the statistical interpretation of entropy would lead us to the same conclusion.

Imagine the container of gas depicted in Figure 22.18a as having all of its molecules traveling at speeds greater than the mean value on the left side and all of its molecules traveling at speeds less than the mean value on the right side (an ordered microstate). Compare this with the uniform mixture of fast- and slow-mov-

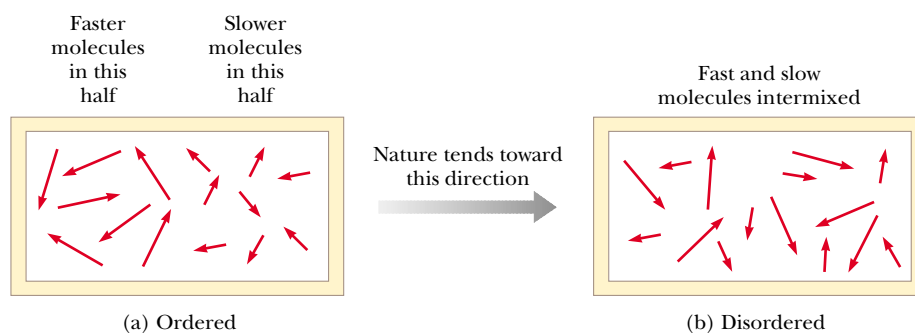


Figure 22.18 A container of gas in two equally probable states of molecular motion. (a) An ordered arrangement, which is one of a few and therefore a collectively unlikely set. (b) A disordered arrangement, which is one of many and therefore a collectively likely set.



Figure 22.19 By tossing a coin into a jar, the carnival-goer can win the fish in the jar. It is more likely that the coin will land in a jar containing a goldfish than in the one containing the black fish.

ing molecules in Figure 22.18b (a disordered microstate). You might expect the ordered microstate to be very unlikely because random motions tend to mix the slow- and fast-moving molecules uniformly. Yet *individually* each of these microstates is equally probable. However, there are far more disordered microstates than ordered microstates, and so a macrostate corresponding to a large number of equivalent disordered microstates is much more probable than a macrostate corresponding to a small number of equivalent ordered microstates.

Figure 22.19 shows a real-world example of this concept. There are two possible macrostates for the carnival game—winning a goldfish and winning a black fish. Because only one jar in the array of jars contains a black fish, only one possible microstate corresponds to the macrostate of winning a black fish. A large number of microstates are described by the coin's falling into a jar containing a goldfish. Thus, for the macrostate of winning a goldfish, there are many equivalent microstates. As a result, the probability of winning a goldfish is much greater than the probability of winning a black fish. If there are 24 goldfish and 1 black fish, the probability of winning the black fish is 1 in 25. This assumes that all microstates have the same probability, a situation that may not be quite true for the situation shown in Figure 22.19. If you are an accurate coin tosser and you are aiming for the edge of the array of jars, then the probability of the coin's landing in a jar near the edge is likely to be greater than the probability of its landing in a jar near the center.

Let us consider a similar type of probability problem for 100 molecules in a container. At any given moment, the probability of one molecule's being in the left part of the container shown in Figure 22.20a as a result of random motion is $\frac{1}{2}$. If there are two molecules, as shown in Figure 22.20b, the probability of both being in the left part is $(\frac{1}{2})^2$ or 1 in 4. If there are three molecules (Fig. 22.20c), the probability of all of them being in the left portion at the same moment is $(\frac{1}{2})^3$, or 1 in 8. For 100 independently moving molecules, the probability that the 50 fastest ones will be found in the left part at any moment is $(\frac{1}{2})^{50}$. Likewise, the probability that the remaining 50 slower molecules will be found in the right part at any moment is $(\frac{1}{2})^{50}$. Therefore, the probability of finding this fast-slow separation as a result of random motion is the product $(\frac{1}{2})^{50}(\frac{1}{2})^{50} = (\frac{1}{2})^{100}$, which corresponds to about 1 in 10^{30} . When this calculation is extrapolated from 100 molecules to the number in 1 mol of gas (6.02×10^{23}), the ordered arrangement is found to be *extremely* improbable!

QuickLab

Roll a pair of dice 100 times and record the total number of spots appearing on the dice for each throw. Which total comes up most frequently? Is this expected?

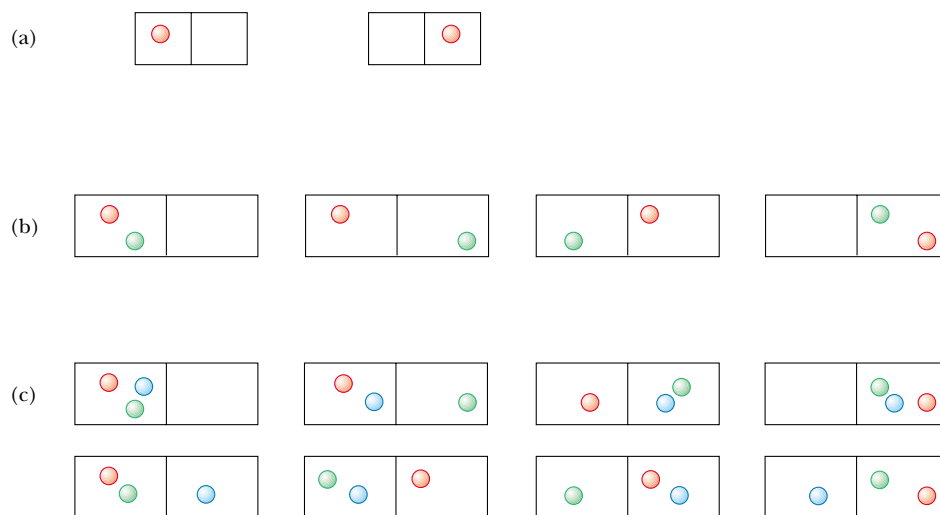


Figure 22.20 (a) One molecule in a two-sided container has a 1-in-2 chance of being on the left side. (b) Two molecules have a 1-in-4 chance of being on the left side at the same time. (c) Three molecules have a 1-in-8 chance of being on the left side at the same time.

EXAMPLE 22.10 Adiabatic Free Expansion—One Last Time

Let us verify that the macroscopic and microscopic approaches to the calculation of entropy lead to the same conclusion for the adiabatic free expansion of an ideal gas. Suppose that 1 mol of gas expands to four times its initial volume. As we have seen for this process, the initial and final temperatures are the same. (a) Using a macroscopic approach, calculate the entropy change for the gas. (b) Using statistical considerations, calculate the change in entropy for the gas and show that it agrees with the answer you obtained in part (a).

Solution (a) Using Equation 22.13, we have

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) = (1)R \ln \left(\frac{4V_i}{V_i} \right) = R \ln 4$$

(b) The number of microstates available to a single molecule in the initial volume V_i is $w_i = V_i/V_m$. For 1 mol (N_A molecules), the number of available microstates is

$$W_i = w_i^{N_A} = \left(\frac{V_i}{V_m} \right)^{N_A}$$

The number of microstates for all N_A molecules in the final volume $V_f = 4V_i$ is

$$W_f = \left(\frac{V_f}{V_m} \right)^{N_A} = \left(\frac{4V_i}{V_m} \right)^{N_A}$$

Thus, the ratio of the number of final microstates to initial microstates is

$$\frac{W_f}{W_i} = 4^{N_A}$$

Using Equation 22.18, we obtain

$$\begin{aligned} \Delta S &= k_B \ln W_f - k_B \ln W_i = k_B \ln \left(\frac{W_f}{W_i} \right) \\ &= k_B \ln(4^{N_A}) = N_A k_B \ln 4 = R \ln 4 \end{aligned}$$

The answer is the same as that for part (a), which dealt with macroscopic parameters.

CONCEPTUAL EXAMPLE 22.11 Let's Play Marbles!

Suppose you have a bag of 100 marbles. Fifty of the marbles are red, and 50 are green. You are allowed to draw four marbles from the bag according to the following rules: Draw one marble, record its color, and return it to the bag. Then draw another marble. Continue this process until you have drawn and returned four marbles. What are the possible

macrostates for this set of events? What is the most likely macrostate? What is the least likely macrostate?

Solution Because each marble is returned to the bag before the next one is drawn, the probability of drawing a red marble is always the same as the probability of drawing a

green one. All the possible microstates and macrostates are shown in Table 22.1. As this table indicates, there is only one way to draw four red marbles, and so there is only one microstate. However, there are four possible microstates that correspond to the macrostate of one green marble and three red marbles; six microstates that correspond to two green marbles and two red marbles; four microstates that corre-

spond to three green marbles and one red marble; and one microstate that corresponds to four green marbles. The most likely macrostate—two red marbles and two green marbles—corresponds to the most disordered microstates. The least likely macrostates—four red marbles or four green marbles—correspond to the most ordered microstates.

TABLE 22.1 Possible Results of Drawing Four Marbles from a Bag

Macrostate	Possible Microstates	Total Number of Microstates
All R	RRRR	1
1G, 3R	RRRG, RRGR, RGRR, GRRR	4
2G, 2R	RRGG, RGRG, GRRG, RGGR, GRGR, GGRR	6
3G, 1R	GGGR, GGRG, GRGG, RGGG	4
All G	GGGG	1

SUMMARY

A **heat engine** is a device that converts internal energy to other useful forms of energy. The net work done by a heat engine in carrying a working substance through a cyclic process ($\Delta E_{\text{int}} = 0$) is

$$W = Q_h - Q_c \quad (22.1)$$

where Q_h is the energy absorbed from a hot reservoir and Q_c is the energy expelled to a cold reservoir.

The **thermal efficiency** e of a heat engine is

$$e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} \quad (22.2)$$

The **second law of thermodynamics** can be stated in the following two ways:

- It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the absorption of energy from a reservoir and the performance of an equal amount of work (the Kelvin–Planck statement).
- It is impossible to construct a cyclic machine whose sole effect is the continuous transfer of energy from one object to another object at a higher temperature without the input of energy by work (the Clausius statement).

In a **reversible** process, the system can be returned to its initial conditions along the same path shown on a PV diagram, and every point along this path is an equilibrium state. A process that does not satisfy these requirements is **irreversible**. **Carnot's theorem** states that no real heat engine operating (irreversibly) between the temperatures T_c and T_h can be more efficient than an engine operating reversibly in a Carnot cycle between the same two temperatures.

The **thermal efficiency** of a heat engine operating in the Carnot cycle is

$$e_C = 1 - \frac{T_c}{T_h} \quad (22.4)$$

You should be able to use this equation (or an equivalent form involving a ratio of heats) to determine the maximum possible efficiency of any heat engine.

The second law of thermodynamics states that when real (irreversible) processes occur, the degree of disorder in the system plus the surroundings increases. When a process occurs in an isolated system, the state of the system becomes more disordered. The measure of disorder in a system is called **entropy** S . Thus, another way in which the second law can be stated is

- The entropy of the Universe increases in all real processes.

The **change in entropy** dS of a system during a process between two infinitesimally separated equilibrium states is

$$dS = \frac{dQ_r}{T} \quad (22.8)$$

where dQ_r is the energy transfer by heat for a reversible process that connects the initial and final states. The change in entropy of a system during an arbitrary process between an initial state and a final state is

$$\Delta S = \int_i^f \frac{dQ_r}{T} \quad (22.9)$$

The value of ΔS for the system is the same for all paths connecting the initial and final states. The change in entropy for a system undergoing any reversible, cyclic process is zero, and when such a process occurs, the entropy of the Universe remains constant.

From a microscopic viewpoint, entropy is defined as

$$S \equiv k_B \ln W \quad (22.18)$$

where k_B is Boltzmann's constant and W is the number of microstates available to the system for the existing macrostate. Because of the statistical tendency of systems to proceed toward states of greater probability and greater disorder, all natural processes are irreversible, and entropy increases. Thus, entropy is a measure of microscopic disorder.

QUESTIONS

1. Is it possible to convert internal energy to mechanical energy? Describe a process in which such a conversion occurs.
2. What are some factors that affect the efficiency of automobile engines?
3. In practical heat engines, which are we able to control more: the temperature of the hot reservoir, or the temperature of the cold reservoir? Explain.
4. A steam-driven turbine is one major component of an electric power plant. Why is it advantageous to have the temperature of the steam as high as possible?
5. Is it possible to construct a heat engine that creates no thermal pollution? What does this tell us about environmental considerations for an industrialized society?
6. Discuss three common examples of natural processes that involve an increase in entropy. Be sure to account for all parts of each system under consideration.
7. Discuss the change in entropy of a gas that expands (a) at constant temperature and (b) adiabatically.
8. In solar ponds constructed in Israel, the Sun's energy is concentrated near the bottom of a salty pond. With the proper layering of salt in the water, convection is prevented, and temperatures of 100°C may be reached. Can you estimate the maximum efficiency with which useful energy can be extracted from the pond?
9. The vortex tube (Fig. Q22.9) is a T-shaped device that takes in compressed air at 20 atm and 20°C and gives off air at -20°C from one flared end and air at 60°C from the other flared end. Does the operation of this device vi-

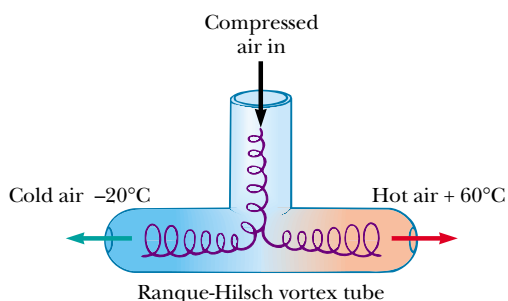


Figure Q22.9

olate the second law of thermodynamics? If not, explain why not.

10. Why does your automobile burn more gas in winter than in summer?
11. Can a heat pump have a coefficient of performance (COP) less than unity? Explain.
12. Give some examples of irreversible processes that occur in nature.
13. Give an example of a process in nature that is nearly reversible.
14. A thermodynamic process occurs in which the entropy of a system changes by -8.0 J/K . According to the second law of thermodynamics, what can you conclude about the entropy change of the environment?
15. If a supersaturated sugar solution is allowed to evaporate slowly, sugar crystals form in the container. Hence, sugar molecules go from a disordered form (in solution) to a highly ordered crystalline form. Does this process violate the second law of thermodynamics? Explain.

16. How could you increase the entropy of 1 mol of a metal that is at room temperature? How could you decrease its entropy?
17. A heat pump is to be installed in a region where the average outdoor temperature in the winter months is -20°C . In view of this, why would it be advisable to place the outdoor compressor unit deep in the ground? Why are heat pumps not commonly used for heating in cold climates?
18. Suppose your roommate is “Mr. Clean” and tidies up your messy room after a big party. That is, your roommate is increasing order in the room. Does this represent a violation of the second law of thermodynamics?
19. Discuss the entropy changes that occur when you (a) bake a loaf of bread and (b) consume the bread.
20. The device shown in Figure Q22.20, which is called a thermoelectric converter, uses a series of semiconductor cells to convert internal energy to electrical energy. In the photograph on the left, both legs of the device are at the same temperature and no electrical energy is produced. However, when one leg is at a higher temperature than the other, as shown in the photograph on the right, electrical energy is produced as the device extracts energy from the hot reservoir and drives a small electric motor. (a) Why does the temperature differential produce electrical energy in this demonstration? (b) In what sense does this intriguing experiment demonstrate the second law of thermodynamics?
21. A classmate tells you that it is just as likely for all the air molecules in the room you are both in to be concentrated in one corner (with the rest of the room being a vacuum) as it is for the air molecules to be distributed uniformly about the room in their current state. Is this true? Why doesn't the situation he describes actually happen?




Figure Q22.20 (Courtesy of PASCO Scientific Company)

PROBLEMS

1, 2, 3 = straightforward, intermediate, challenging □ = full solution available in the *Student Solutions Manual and Study Guide*

WEB = solution posted at <http://www.saunderscollege.com/physics/>  = Computer useful in solving problem  = Interactive Physics

 = paired numerical/symbolic problems

Section 22.1 Heat Engines and the Second Law of Thermodynamics

Section 22.2 Reversible and Irreversible Processes

1. A heat engine absorbs 360 J of energy and performs 25.0 J of work in each cycle. Find (a) the efficiency of the engine and (b) the energy expelled to the cold reservoir in each cycle.
2. The energy absorbed by an engine is three times greater than the work it performs. (a) What is its thermal efficiency? (b) What fraction of the energy absorbed is expelled to the cold reservoir?
3. A particular engine has a power output of 5.00 kW and an efficiency of 25.0%. Assuming that the engine expels 8 000 J of energy in each cycle, find (a) the energy absorbed in each cycle and (b) the time for each cycle.
4. A heat engine performs 200 J of work in each cycle and has an efficiency of 30.0%. For each cycle, how much energy is (a) absorbed and (b) expelled?
5. An ideal gas is compressed to half its original volume while its temperature is held constant. (a) If 1 000 J of energy is removed from the gas during the compression, how much work is done on the gas? (b) What is the change in the internal energy of the gas during the compression?
6. Suppose that a heat engine is connected to two energy reservoirs, one a pool of molten aluminum (660°C) and the other a block of solid mercury (−38.9°C). The engine runs by freezing 1.00 g of aluminum and melting 15.0 g of mercury during each cycle. The heat of fusion of aluminum is 3.97×10^5 J/kg; the heat of fusion of mercury is 1.18×10^4 J/kg. What is the efficiency of this engine?

Section 22.3 The Carnot Engine

7. One of the most efficient engines ever built (actual efficiency 42.0%) operates between 430°C and 1 870°C. (a) What is its maximum theoretical efficiency? (b) How much power does the engine deliver if it absorbs 1.40×10^5 J of energy each second from the hot reservoir?
8. A heat engine operating between 80.0°C and 200°C achieves 20.0% of the maximum possible efficiency. What energy input will enable the engine to perform 10.0 kJ of work?
9. A Carnot engine has a power output of 150 kW. The engine operates between two reservoirs at 20.0°C and 500°C. (a) How much energy does it absorb per hour? (b) How much energy is lost per hour in its exhaust?
10. A steam engine is operated in a cold climate where the exhaust temperature is 0°C. (a) Calculate the theoreti-

cal maximum efficiency of the engine, using an intake steam temperature of 100°C. (b) If superheated steam at 200°C were used instead, what would be the maximum possible efficiency?

11. An ideal gas is taken through a Carnot cycle. The isothermal expansion occurs at 250°C, and the isothermal compression takes place at 50.0°C. Assuming that the gas absorbs 1 200 J of energy from the hot reservoir during the isothermal expansion, find (a) the energy expelled to the cold reservoir in each cycle and (b) the net work done by the gas in each cycle.
12. The exhaust temperature of a Carnot heat engine is 300°C. What is the intake temperature if the efficiency of the engine is 30.0%?
13. A power plant operates at 32.0% efficiency during the summer when the sea water for cooling is at 20.0°C. The plant uses 350°C steam to drive turbines. Assuming that the plant's efficiency changes in the same proportion as the ideal efficiency, what would be the plant's efficiency in the winter, when the sea water is at 10.0°C?
14. Argon enters a turbine at a rate of 80.0 kg/min, a temperature of 800°C, and a pressure of 1.50 MPa. It expands adiabatically as it pushes on the turbine blades and exits at a pressure of 300 kPa. (a) Calculate its temperature at the time of exit. (b) Calculate the (maximum) power output of the turning turbine. (c) The turbine is one component of a model closed-cycle gas turbine engine. Calculate the maximum efficiency of the engine.
15. A power plant that would make use of the temperature gradient in the ocean has been proposed. The system is to operate between 5.00°C (water temperature at a depth of about 1 km) and 20.0°C (surface water temperature). (a) What is the maximum efficiency of such a system? (b) If the power output of the plant is 75.0 MW, how much energy is absorbed per hour? (c) In view of your answer to part (a), do you think such a system is worthwhile (considering that there is no charge for fuel)?
16. A 20.0%-efficient real engine is used to speed up a train from rest to 5.00 m/s. It is known that an ideal (Carnot) engine having the same cold and hot reservoirs would accelerate the same train from rest to a speed of 6.50 m/s using the same amount of fuel. Assuming that the engines use air at 300 K as a cold reservoir, find the temperature of the steam serving as the hot reservoir.
17. A firebox is at 750 K, and the ambient temperature is 300 K. The efficiency of a Carnot engine doing 150 J of work as it transports energy between these constant-temperature baths is 60.0%. The Carnot engine must absorb energy $150 \text{ J} / 0.600 = 250 \text{ J}$ from the hot reser-

voir and release 100 J of energy into the environment. To follow Carnot's reasoning, suppose that some other heat engine S could have an efficiency of 70.0%.

(a) Find the energy input and energy output of engine S as it does 150 J of work. (b) Let engine S operate as in part (a) and run the Carnot engine in reverse. Find the total energy the firebox puts out as both engines operate together and the total energy absorbed by the environment. Show that the Clausius statement of the second law of thermodynamics is violated. (c) Find the energy input and work output of engine S as it exhausts 100 J of energy. (d) Let engine S operate as in (c) and contribute 150 J of its work output to running the Carnot engine in reverse. Find the total energy that the firebox puts out as both engines operate together, the total work output, and the total energy absorbed by the environment. Show that the Kelvin–Planck statement of the second law is violated. Thus, our assumption about the efficiency of engine S must be false. (e) Let the engines operate together through one cycle as in part (d). Find the change in entropy of the Universe. Show that the entropy statement of the second law is violated.

18. At point A in a Carnot cycle, 2.34 mol of a monatomic ideal gas has a pressure of 1 400 kPa, a volume of 10.0 L, and a temperature of 720 K. It expands isothermally to point B, and then expands adiabatically to point C, where its volume is 24.0 L. An isothermal compression brings it to point D, where its new volume is 15.0 L. An adiabatic process returns the gas to point A. (a) Determine all the unknown pressures, volumes, and temperatures as you fill in the following table:

	<i>P</i>	<i>V</i>	<i>T</i>
A	1 400 kPa	10.0 L	720 K
B			
C		24.0 L	
D		15.0 L	

(b) Find the energy added by heat, the work done, and the change in internal energy for each of the following steps: $A \rightarrow B$, $B \rightarrow C$, $C \rightarrow D$, and $D \rightarrow A$. (c) Show that $W_{\text{net}}/Q_{\text{in}} = 1 - T_C/T_A$, the Carnot efficiency.

Section 22.4 Gasoline and Diesel Engines

19. In a cylinder of an automobile engine just after combustion, the gas is confined to a volume of 50.0 cm³ and has an initial pressure of 3.00×10^6 Pa. The piston moves outward to a final volume of 300 cm³, and the gas expands without energy loss by heat. (a) If $\gamma = 1.40$ for the gas, what is the final pressure? (b) How much work is done by the gas in expanding?
20. A gasoline engine has a compression ratio of 6.00 and uses a gas for which $\gamma = 1.40$. (a) What is the efficiency of the engine if it operates in an idealized Otto cycle?

(b) If the actual efficiency is 15.0%, what fraction of the fuel is wasted as a result of friction and energy losses by heat that could be avoided in a reversible engine? (Assume complete combustion of the air–fuel mixture.)

21. A 1.60-L gasoline engine with a compression ratio of 6.20 has a power output of 102 hp. Assuming that the engine operates in an idealized Otto cycle, find the energy absorbed and exhausted each second. Assume that the fuel–air mixture behaves like an ideal gas, with $\gamma = 1.40$.
22. The compression ratio of an Otto cycle, as shown in Figure 22.12, is $V_A/V_B = 8.00$. At the beginning A of the compression process, 500 cm³ of gas is at 100 kPa and 20.0°C. At the beginning of the adiabatic expansion, the temperature is $T_C = 750^\circ\text{C}$. Model the working fluid as an ideal gas, with $E_{\text{int}} = nC_VT = 2.50nRT$ and $\gamma = 1.40$. (a) Fill in the following table to track the states of the gas:

	<i>T</i> (K)	<i>P</i> (kPa)	<i>V</i> (cm ³)	<i>E</i> _{int}
A	293	100	500	
B				
C	1 023			
D				
A				

(b) Fill in the following table to track the processes:

	<i>Q</i>	<i>W</i>	ΔE_{int}
$A \rightarrow B$			
$B \rightarrow C$			
$C \rightarrow D$			
$D \rightarrow A$			
ABCD			

(c) Identify the energy input Q_h , the energy exhaust Q_c , and the net output work W . (d) Calculate the thermal efficiency. (e) Find the number of revolutions per minute that the crankshaft must complete for a one-cylinder engine to have an output power of 1.00 kW = 1.34 hp. (*Hint:* The thermodynamic cycle involves four piston strokes.)

Section 22.5 Heat Pumps and Refrigerators

23. What is the coefficient of performance of a refrigerator that operates with Carnot efficiency between the temperatures -3.00°C and $+27.0^\circ\text{C}$?
24. What is the maximum possible coefficient of performance of a heat pump that brings energy from outdoors at -3.00°C into a 22.0°C house? (*Hint:* The heat pump does work W , which is also available to warm up the house.)

- 25.** An ideal refrigerator or ideal heat pump is equivalent to a Carnot engine running in reverse. That is, energy Q_c is absorbed from a cold reservoir, and energy Q_h is rejected to a hot reservoir. (a) Show that the work that must be supplied to run the refrigerator or heat pump is

$$W = \frac{T_h - T_c}{T_c} Q_c$$

(b) Show that the coefficient of performance (COP) of the ideal refrigerator is

$$\text{COP} = \frac{T_c}{T_h - T_c}$$

- 26.** A heat pump (Fig. P22.26) is essentially a heat engine run backward. It extracts energy from colder air outside and deposits it in a warmer room. Suppose that the ratio of the actual energy entering the room to the work done by the device's motor is 10.0% of the theoretical maximum ratio. Determine the energy entering the room per joule of work done by the motor when the inside temperature is 20.0°C and the outside temperature is -5.00°C .

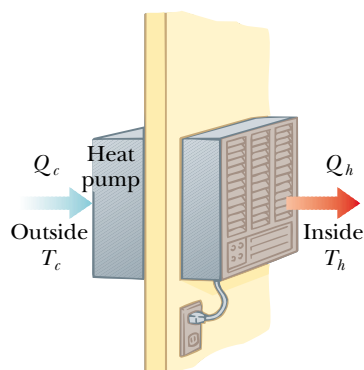


Figure P22.26

- WEB 27.** How much work does an ideal Carnot refrigerator require to remove 1.00 J of energy from helium at 4.00 K and reject this energy to a room-temperature (293-K) environment?
- 28.** How much work does an ideal Carnot refrigerator require to remove energy Q from helium at T_c and reject this energy to a room-temperature environment at T_h ?
- 29.** A refrigerator has a coefficient of performance equal to 5.00. Assuming that the refrigerator absorbs 120 J of energy from a cold reservoir in each cycle, find (a) the work required in each cycle and (b) the energy expelled to the hot reservoir.
- 30.** A refrigerator maintains a temperature of 0°C in the cold compartment with a room temperature of 25.0°C . It removes energy from the cold compartment at the rate 8 000 kJ/h. (a) What minimum power is required

to operate the refrigerator? (b) At what rate does the refrigerator exhaust energy into the room?

Section 22.6 Entropy

- 31.** An ice tray contains 500 g of water at 0°C . Calculate the change in entropy of the water as it freezes slowly and completely at 0°C .
- 32.** At a pressure of 1 atm, liquid helium boils at 4.20 K. The latent heat of vaporization is 20.5 kJ/kg. Determine the entropy change (per kilogram) of the helium resulting from vaporization.
- 33.** Calculate the change in entropy of 250 g of water heated slowly from 20.0°C to 80.0°C . (Hint: Note that $dQ = mc dT$.)
- 34.** An airtight freezer holds 2.50 mol of air at 25.0°C and 1.00 atm. The air is then cooled to -18.0°C . (a) What is the change in entropy of the air if the volume is held constant? (b) What would the change be if the pressure were maintained at 1 atm during the cooling?

Section 22.7 Entropy Changes in Irreversible Processes

- 35.** The temperature at the surface of the Sun is approximately 5 700 K, and the temperature at the surface of the Earth is approximately 290 K. What entropy change occurs when 1 000 J of energy is transferred by radiation from the Sun to the Earth?
- 36.** A 1.00-kg iron horseshoe is taken from a furnace at 900°C and dropped into 4.00 kg of water at 10.0°C . Assuming that no energy is lost by heat to the surroundings, determine the total entropy change of the system (horseshoe and water).
- WEB 37.** A 1 500-kg car is moving at 20.0 m/s. The driver brakes to a stop. The brakes cool off to the temperature of the surrounding air, which is nearly constant at 20.0°C . What is the total entropy change?
- 38.** How fast are you personally making the entropy of the Universe increase right now? Make an order-of-magnitude estimate, stating what quantities you take as data and the values you measure or estimate for them.
- 39.** One mole of H_2 gas is contained in the left-hand side of the container shown in Figure P22.39, which has equal volumes left and right. The right-hand side is evacuated. When the valve is opened, the gas streams into the right-hand side. What is the final entropy change of the gas? Does the temperature of the gas change?

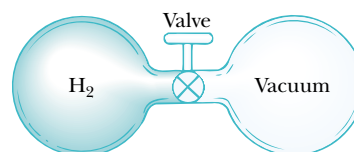


Figure P22.39

- 40.** A rigid tank of small mass contains 40.0 g of argon, initially at 200°C and 100 kPa. The tank is placed into a reservoir at 0°C and is allowed to cool to thermal equi-

librium. Calculate (a) the volume of the tank, (b) the change in internal energy of the argon, (c) the energy transferred by heat, (d) the change in entropy of the argon, and (e) the change in entropy of the constant-temperature bath.

41. A 2.00-L container has a center partition that divides it into two equal parts, as shown in Figure P22.41. The left-hand side contains H_2 gas, and the right-hand side contains O_2 gas. Both gases are at room temperature and at atmospheric pressure. The partition is removed, and the gases are allowed to mix. What is the entropy increase of the system?

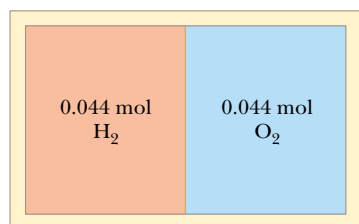


Figure P22.41

42. A 100 000-kg iceberg at -5.00°C breaks away from the polar ice shelf and floats away into the ocean, at 5.00°C . What is the final change in the entropy of the system after the iceberg has completely melted? (The specific heat of ice is $2010 \text{ J/kg} \cdot ^\circ\text{C}$.)
43. One mole of an ideal monatomic gas, initially at a pressure of 1.00 atm and a volume of 0.0250 m^3 , is heated to a final state with a pressure of 2.00 atm and a volume of 0.0400 m^3 . Determine the change in entropy of the gas for this process.
44. One mole of a diatomic ideal gas, initially having pressure P and volume V , expands so as to have pressure $2P$ and volume $2V$. Determine the entropy change of the gas in the process.

(Optional)

Section 22.8 Entropy on a Microscopic Scale

45. If you toss two dice, what is the total number of ways in which you can obtain (a) a 12 and (b) a 7?
46. Prepare a table like Table 22.1 for the following occurrence. You toss four coins into the air simultaneously and then record the results of your tosses in terms of the numbers of heads and tails that result. For example, HHTH and HTHH are two possible ways in which three heads and one tail can be achieved. (a) On the basis of your table, what is the most probable result of a toss? In terms of entropy, (b) what is the most ordered state, and (c) what is the most disordered?
47. Repeat the procedure used to construct Table 22.1 (a) for the case in which you draw three marbles from your bag rather than four and (b) for the case in which you draw five rather than four.

ADDITIONAL PROBLEMS

48. Every second at Niagara Falls, some $5\,000 \text{ m}^3$ of water falls a distance of 50.0 m (Fig. P22.48). What is the increase in entropy per second due to the falling water? (Assume that the mass of the surroundings is so great that its temperature and that of the water stay nearly constant at 20.0°C . Suppose that a negligible amount of water evaporates.)



Figure P22.48 Niagara Falls. (Jan Kopec/Tony Stone Images)

49. If a 35.0%-efficient Carnot heat engine is run in reverse so that it functions as a refrigerator, what would be the engine's (that is, the refrigerator's) coefficient of performance (COP)?
50. How much work does an ideal Carnot refrigerator use to change 0.500 kg of tap water at 10.0°C into ice at -20.0°C ? Assume that the freezer compartment is held at -20.0°C and that the refrigerator exhausts energy into a room at 20.0°C .
- WEB 51. A house loses energy through the exterior walls and roof at a rate of $5\,000 \text{ J/s} = 5.00 \text{ kW}$ when the interior temperature is 22.0°C and the outside temperature is -5.00°C . Calculate the electric power required to maintain the interior temperature at 22.0°C for the following two cases: (a) The electric power is used in electric resistance heaters (which convert all of the electricity supplied into internal energy). (b) The electric power is used to drive an electric motor that operates the compressor of a heat pump (which has a coefficient of performance [COP] equal to 60.0% of the Carnot-cycle value).
52. A heat engine operates between two reservoirs at $T_2 = 600 \text{ K}$ and $T_1 = 350 \text{ K}$. It absorbs $1\,000 \text{ J}$ of energy from the higher-temperature reservoir and performs 250 J of work. Find (a) the entropy change of the Universe ΔS_U for this process and (b) the work W that could have been done by an ideal Carnot engine operating between these two reservoirs. (c) Show that the difference between the work done in parts (a) and (b) is $T_1 \Delta S_U$.
- WEB 53. Figure P22.53 represents n mol of an ideal monatomic gas being taken through a cycle that consists of two isothermal processes at temperatures $3T_i$ and T_i and two constant-volume processes. For each cycle, determine,

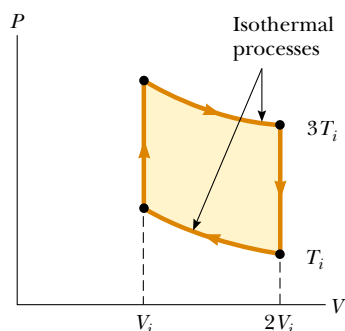


Figure P22.53

in terms of n , R , and T_i , (a) the net energy transferred by heat to the gas and (b) the efficiency of an engine operating in this cycle.

54. A refrigerator has a coefficient of performance (COP) of 3.00. The ice tray compartment is at -20.0°C , and the room temperature is 22.0°C . The refrigerator can convert 30.0 g of water at 22.0°C to 30.0 g of ice at -20.0°C each minute. What input power is required? Give your answer in watts.
55. An ideal (Carnot) freezer in a kitchen has a constant temperature of 260 K, while the air in the kitchen has a constant temperature of 300 K. Suppose that the insulation for the freezer is not perfect, such that some energy flows into the freezer at a rate of 0.150 W. Determine the average power that the freezer's motor needs to maintain the constant temperature in the freezer.
56. An electric power plant has an overall efficiency of 15.0%. The plant is to deliver 150 MW of power to a city, and its turbines use coal as the fuel. The burning coal produces steam, which drives the turbines. The steam is then condensed to water at 25.0°C as it passes through cooling coils in contact with river water. (a) How many metric tons of coal does the plant consume each day (1 metric ton = 10^3 kg)? (b) What is the total cost of the fuel per year if the delivered price is \$8.00/metric ton? (c) If the river water is delivered at 20.0°C , at what minimum rate must it flow over the cooling coils in order that its temperature not exceed 25.0°C ? (Note: The heat of combustion of coal is 33.0 kJ/g.)

57. A power plant, having a Carnot efficiency, produces 1 000 MW of electrical power from turbines that take in steam at 500 K and reject water at 300 K into a flowing river. Assuming that the water downstream is 6.00 K warmer due to the output of the power plant, determine the flow rate of the river.
58. A power plant, having a Carnot efficiency, produces electric power \mathcal{P} from turbines that take in energy from steam at temperature T_h and discharge energy at temperature T_c through a heat exchanger into a flowing river. Assuming that the water downstream is warmer by ΔT due to the output of the power plant, determine the flow rate of the river.

59. An athlete whose mass is 70.0 kg drinks 16 oz (453.6 g) of refrigerated water. The water is at a temperature of 35.0°F . (a) Neglecting the temperature change of her body that results from the water intake (that is, the body is regarded as a reservoir that is always at 98.6°F), find the entropy increase of the entire system. (b) Assume that the entire body is cooled by the drink and that the average specific heat of a human is equal to the specific heat of liquid water. Neglecting any other energy transfers by heat and any metabolic energy release, find the athlete's temperature after she drinks the cold water, given an initial body temperature of 98.6°F . Under these assumptions, what is the entropy increase of the entire system? Compare this result with the one you obtained in part (a).
60. One mole of an ideal monatomic gas is taken through the cycle shown in Figure P22.60. The process $A \rightarrow B$ is a reversible isothermal expansion. Calculate (a) the net work done by the gas, (b) the energy added to the gas, (c) the energy expelled by the gas, and (d) the efficiency of the cycle.

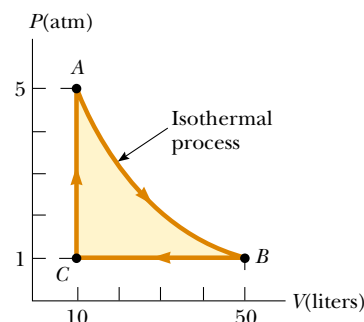


Figure P22.60

61. Calculate the increase in entropy of the Universe when you add 20.0 g of 5.00°C cream to 200 g of 60.0°C coffee. Assume that the specific heats of cream and coffee are both 4.20 J/g $^\circ\text{C}$.
62. In 1993 the federal government instituted a requirement that all room air conditioners sold in the United States must have an energy efficiency ratio (EER) of 10 or higher. The EER is defined as the ratio of the cooling capacity of the air conditioner, measured in Btu/h, to its electrical power requirement in watts. (a) Convert the EER of 10.0 to dimensionless form, using the conversion 1 Btu = $1\,055$ J. (b) What is the appropriate name for this dimensionless quantity? (c) In the 1970s it was common to find room air conditioners with EERs of 5 or lower. Compare the operating costs for 10 000-Btu/h air conditioners with EERs of 5.00 and 10.0 if each air conditioner were to operate for 1 500 h during the summer in a city where electricity costs 10.0¢ per kilowatt-hour.

63. One mole of a monatomic ideal gas is taken through the cycle shown in Figure P22.63. At point A, the pressure, volume, and temperature are P_i , V_i , and T_i , respectively. In terms of R and T_i , find (a) the total energy entering the system by heat per cycle, (b) the total energy leaving the system by heat per cycle, (c) the efficiency of an engine operating in this cycle, and (d) the efficiency of an engine operating in a Carnot cycle between the same temperature extremes.

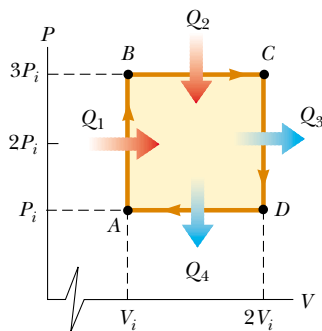


Figure P22.63

64. One mole of an ideal gas expands isothermally. (a) If the gas doubles its volume, show that the work of expansion is $W = RT \ln 2$. (b) Because the internal energy E_{int} of an ideal gas depends solely on its temperature, no change in E_{int} occurs during the expansion. It follows from the first law that the heat input to the gas during the expansion is equal to the energy output by work. Why does this conversion *not* violate the second law?
65. A system consisting of n mol of an ideal gas undergoes a reversible, *isobaric* process from a volume V_i to a volume $3V_i$. Calculate the change in entropy of the gas. (*Hint*: Imagine that the system goes from the initial state to the final state first along an isotherm and then along an adiabatic path—no change in entropy occurs along the adiabatic path.)
66. Suppose you are working in a patent office, and an inventor comes to you with the claim that her heat engine, which employs water as a working substance, has a thermodynamic efficiency of 0.61. She explains that it operates between energy reservoirs at 4°C and 0°C . It is a very complicated device, with many pistons, gears, and pulleys, and the cycle involves freezing and melting. Does her claim that $e = 0.61$ warrant serious consideration? Explain.
67. An idealized diesel engine operates in a cycle known as the *air-standard diesel cycle*, as shown in Figure 22.13. Fuel is sprayed into the cylinder at the point of maximum compression B . Combustion occurs during the expansion $B \rightarrow C$, which is approximated as an isobaric process. Show that the efficiency of an engine operating in this idealized diesel cycle is
- $$e = 1 - \frac{1}{\gamma} \left(\frac{T_D - T_A}{T_C - T_B} \right)$$
68. One mole of an ideal gas ($\gamma = 1.40$) is carried through the Carnot cycle described in Figure 22.10. At point A, the pressure is 25.0 atm and the temperature is 600 K. At point C, the pressure is 1.00 atm and the temperature is 400 K. (a) Determine the pressures and volumes at points A, B, C, and D. (b) Calculate the net work done per cycle. (c) Determine the efficiency of an engine operating in this cycle.
69. A typical human has a mass of 70.0 kg and produces about 2 000 kcal (2.00×10^6 cal) of metabolic energy per day. (a) Find the rate of metabolic energy production in watts and in calories per hour. (b) If none of the metabolic energy were transferred out of the body, and the specific heat of the human body is $1.00 \text{ cal/g} \cdot ^\circ\text{C}$, what is the rate at which body temperature would rise? Give your answer in degrees Celsius per hour and in degrees Fahrenheit per hour.
70. Suppose that 1.00 kg of water at 10.0°C is mixed with 1.00 kg of water at 30.0°C at constant pressure. When the mixture has reached equilibrium, (a) what is the final temperature? (b) Take $c_p = 4.19 \text{ kJ/kg} \cdot \text{K}$ for water. Show that the entropy of the system increases by
- $$\Delta S = 4.19 \ln \left[\left(\frac{293}{283} \right) \left(\frac{293}{303} \right) \right] \text{ kJ/K}$$
- (c) Verify numerically that $\Delta S > 0$. (d) Is the mixing an irreversible process?

ANSWERS TO QUICK QUIZZES

- 22.1 The cost of heating your home decreases to 25% of the original cost. With electric heating, you receive the same amount of energy for heating your home as enters it by electricity. The COP of 4 for the heat pump means that you are receiving four times as much energy as the energy entering by electricity. With four times as much energy per unit of energy from electricity, you need only one-fourth as much electricity.
- 22.2 (b) Because the process is reversible and adiabatic, $Q_r = 0$; therefore, $\Delta S = 0$.

- 22.3 False. The second law states that the entropy of the *Universe* increases in real processes. Although the organization of molecules into ordered leaves and branches represents a decrease in entropy *of the tree*, this organization takes place because of a number of processes in which the tree interacts with its surroundings. If we include the entropy changes associated with all these processes, the entropy change of the Universe during the growth of a tree is still positive.